

PAINTING ON GLASS

AND PORCELAIN

FELIX HERMANN



3 1761 06706098 8

PUBLISHED AT THE OFFICES OF
"THE POTTERY GAZETTE"



Presented to
The Library
of the
University of Toronto
by
Mrs. W. R. Lang



Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

TC
H
PAINTING ON GLASS AND PORCELAIN

AND

ENAMEL PAINTING

A COMPLETE INTRODUCTION TO THE PREPARATION OF ALL
THE COLOURS AND FLUXES USED FOR PAINTING ON GLASS,
PORCELAIN, ENAMEL, FAIENCE AND STONEWARE, THE
COLOUR PASTES AND COLOURED GLASSES, TOGETHER
WITH A MINUTE DESCRIPTION OF THE FIRING
OF COLOURS AND ENAMELS

*ON THE BASIS OF PERSONAL PRACTICAL EXPERIENCE
OF THE CONDITION OF THE ART UP TO DATE*

BY

FELIX HERMANN

TECHNICAL CHEMIST

WITH 18 ILLUSTRATIONS

SECOND, GREATLY ENLARGED, EDITION

TRANSLATED BY

CHARLES SALTER

378540
10.4.40

LONDON

SCOTT, GREENWOOD, & CO.

PUBLISHERS OF THE

Potters Gazette

19, 21, AND 23 LUDGATE HILL, CITY, E.C.

1897

THE UNIVERSITY OF ABERDEEN

ABERDEEN UNIVERSITY PRESS

PREFACE.

IN the preface to the first edition I remarked that, so far as my knowledge extended, there was no other independent work on the production of the colours for glass and porcelain painting, *i.e.*, the chemical and mechanical preparation of the pigments and metals necessary for this class of painting, except, perhaps, Brongniart's *Traité des Arts Céramiques*, which is now out of date. There are, it is true, a few works on the subject in the German language, but these are, for the most part, uncritical compilations of essays on glass and porcelain colours, and contain recipes and instructions which I have personally found to be unreliable.

My own practical experience in the subject, which I was able to complete in the celebrated manufactory at Sèvres, has placed me in a position to produce a complete work on the whole matter, and one that I feel will, in view of the facts referred to above, supply an existing deficiency and be welcomed both by amateurs and by those engaged in the business.

In preparing the first edition I naturally endeavoured to include everything that was, in my opinion, of importance to our subject, whilst giving only those instructions of whose practicability I had been able to convince myself by personal investi-

gation. In the course of the years that have since elapsed, many novelties have been brought out in this connection, few of which, however, possess any actual practical value. This necessitated a careful sifting of the materials at disposal in order to exclude superfluities and useless matter, and maintain the value of the book for the practical man. The residue of actually valuable material was, however, so great as to render the enlargement of the work necessary.

Since the manufacture of the coloured glass pastes and the production of coloured glasses stands in close connection with that of the glass colours, exhaustive treatises on these matters have been incorporated, and the technical side of glass painting thoroughly depicted.

The undersigned therefore hopes that his work, in this new and greatly enlarged edition, will constitute a reliable and profitable guide to all who are engaged in the beautiful branches of industrial art treated of in its pages.

THE AUTHOR.

TABLE OF CONTENTS.

CHAPTER	PAGE
PREFACE	iii
INTRODUCTION--	
History of glass painting	1
I. THE ARTICLES TO BE PAINTED--	
Glass	11
Porcelain	14
Enamel	17
Stoneware	19
Faience	20
II. PIGMENTS--	
1. METALLIC PIGMENTS	22
Antimony oxide	22
Naples yellow	23
Barium chromate	25
Lead chromate	26
Silver chloride	27
Chromic oxide	29
1. Potassium bichromate and sulphur method	29
2. Ammonium chromate method	31
3. Wet method	31
4. Mercurous nitrate and potassium bichromate method	32
Iron Oxide	34
1. Preparation of ferric oxide from ferrous sulphate	36
2. Ferric oxide for fine (red) colours	38
3. Vogel's iron red	40
Ferrous chromate	40
Gold purple	41
Iridium oxide	46
Copper oxide	48
Copper protoxide	49
Cobalt oxide	51
Cobaltous silicate	55
Cobaltous zinc phosphate	56
Smalt	57
Zaffre	59

CHAPTER	PAGE
Manganese oxide	60
Uranium oxide	62
Zinc oxide	63
Tin oxide	66
2. EARTHY COLOURS	68
Yellow ochre	68
Red ochre	70
Terra di Sienna	70
Umber	71
Mars yellow	71
3. METALS	73
Gold	73
Mussel gold	74
Mussel silver	76
Platinum	77
III. FLUXES—	
Fluxes	79
Felspar	80
Quartz	81
Purifying quartz	84
Sedimentation	85
Quenching	86
Borax	87
Boracic acid	88
Potassium and sodium carbonates	88
Rocaille flux	89
IV. PREPARATION OF THE COLOURS FOR GLASS PAINTING—	
1. Black	90
2. White	93
3. Red	95
4. Yellow	101
5. Green	107
6. Violet	111
7. Blue	117
8. Brown	123
Fluxes	127
V. THE COLOUR PASTES	132
VI. THE COLOURED GLASSES—	
Behaviour of glass in presence of metals and metallic oxides	139
Yellow-coloured glass	141
Brown-coloured glass	142
Blue-coloured glass	143
Green-coloured glass	143
Red-coloured glass	144

CHAPTER	PAGE
Gold ruby glass (according to Fuss)	145
Copper ruby glass	146
Lead-free (flash) glass	147
Lead-ruby glass	147
Violet-coloured glass	148
Black glass	148
VII. COMPOSITION OF THE PORCELAIN COLOURS.	149
1. Soft muffle colours	152
2. Hard muffle colours	186
3. Colours for strong fire	189
VIII. THE ENAMEL COLOURS.	216
Enamels for artistic work	223
IX. METALLIC ORNAMENTATION—	
Porcelain gilding	230
Glass gilding	236
X. FIRING THE COLOURS—	
1. Remarks on firing	244
Firing colours on glass	244
Firing colours on porcelain	248
2. The Muffle	253
XI. ACCIDENTS OCCASIONALLY SUPERVENING DURING THE PROCESS OF FIRING	275
XII. REMARKS ON THE DIFFERENT METHODS OF PAINTING ON GLASS, PORCELAIN, ETC.	282
APPENDIX—	
Cleaning old glass paintings	295
INDEX	297

PAINTING ON GLASS AND PORCELAIN.

INTRODUCTION.

HISTORY OF GLASS PAINTING.

ALTHOUGH in the subjoined historical particulars the data handed down to us have been adhered to, we consider it, nevertheless, important to make thereon a few preliminary observations, which, indeed, involuntarily thrust themselves upon one's mind when visiting large museums. In the Egyptian collections in these museums we find a large number of objects presenting an indubitable proof that the Egyptians who lived 4000 years ago were already masters of the art of producing white and coloured glass and of glass smelting. On this account it is not improbable that they also understood how to apply certain permanent colours to individual portions of glass surfaces, thereby laying the foundation of the technical industry of glass painting.

However, the art (in the true sense of the word) of painting on glass is very young, since it was only in recent times that it was brought to the state in which we now see it, although the commencement of the art decidedly dates back as far as the first centuries of our era.

The invention of true glass painting was made in the eleventh century. The ancients, however, were acquainted with the art of preparing their multi-coloured household and decorative articles by fusing together portions of glass coloured in the soft stage, as is shown clearly enough in the

numerous specimens of Roman glass ware extant, such as beads, vases, urns, tear bottles, etc. Still, at that time, the use of glass for windows was as yet unknown, and, therefore, "glass painting" in its true meaning cannot be considered as being then existent.

The ordinary window glass, of which we first discover undoubted traces in the fourth century of the Christian era, differed materially in its nature from that of the present day. It was only made in small irregular panes of considerable, though unequal, thickness, and yellowish (bottle) green in colour. Already, in the ninth century, a similar coloured glass was used in Rome for covering the windows of churches. This was, however, effected only by a purely chromatic grouping of dark coloured glasses in leaden frames. Subsequently the individual panes were arranged in symmetrical order after the style of mosaics; and finally, by the juxtaposition of suitable coloured glasses cut to shape, pictures were produced, but it was only at a much later period that these cut pieces were provided with outlines, and more or less shading, by means of vitrified metallic colours fired into the surface of the glass.

Only a single pigment, the so-called "black flux"—a brownish black, surface colour—was at the disposal of the artist on glass in those days. Some highly interesting information on the technical processes of the oldest glass painters is afforded by Theophilus Presbyter in his eleventh century treatise, *Diversum Artium Schedulæ*, lib. ii. The glass painter of that day had not only to prepare his own colours and designs, but also to make and cut the glass himself. After the latter had been prepared he proceeded with the preliminaries for the operation of painting. In the first place a wooden table of the size of the projected window was made, the entire surface of which was rubbed over with chalk, moistened with water, evenly distributed by the

aid of a cloth, and left to dry. On this table a sketch in outline of the picture was drawn with red or black colour, or with lead or tin, the different colours being indicated by letters, and in this way various divisions were mapped out and covered with sheets of glass of corresponding size. In order to make the glass sheets agree as closely as possible in size with the divisions, the outlines, visible through the glass, were traced thereon in white, and the glass cut along the tracing by means of a glowing iron, the edges being thereafter smoothed with a large iron (*grosarium ferrum*); and then only were the various pieces placed together for the purpose of being painted. The "black flux"—a combination of copper scale with green and blue lead glass—served as pigment, and the painter drew therewith the interior contour of his design. The shading was produced by careful cross-hatching; where light was desired the glass was left transparent. Damascened effects were produced, according to the artist's fancy, on garments and backgrounds, by lightly sizing the glass and removing as much of the coating, by means of an etching tool, as sufficed to produce various kinds of patterns.

For the process of firing the colours (chapter xxii.) several rods were stuck into the ground in a corner of the house, and the equal sized ends of each pair were bound together into an arch about eighteen inches high and the same breadth. This framework, some two feet or more in length, was plastered over on the inside and outside, about four inches thick, with a mixture of three parts of potters' clay and one part of horse dung well soaked with water and mixed with dry hay. A smoke-hole of about a handbreadth was left open at the top, and a doorway in front, as well as three corresponding apertures in each side, the latter large enough to permit of the insertion of iron rods as thick as a man's thumb. A fire was kept burning in this furnace until

the walls were perfectly dry, and then an iron plate, two fingers' breadth shorter and narrower than the dimensions of the oven, was prepared and fitted with a handle. A thick layer of dry or quick lime having been spread over this plate and levelled down by a flat piece of wood, the painted plates of glass were laid side by side thereon, so that the green and blue pieces lay on the outside, and the more refractory white, yellow and red pieces in the centre. The plate was then placed over the iron cross-pieces, and a moderate fire of beechwood lighted, which was gradually increased until the flames rose around the sides of the plate and met above the glass. As soon as the latter began to glow the fire was quickly drawn, and, the openings being covered up, the furnace left alone until cooled down. On taking the glass out it was tested with the nail to see if the colour would scratch off. If it resisted, the operation was finished; otherwise the firing had to be repeated.

The next step was to lay the coloured pieces in proper order on the wooden cartoon, and join them together with strips of lead, after which the whole was enclosed in a wooden frame.

The oldest monumental buildings which have transmitted glass remains (veritable glass samples) to our own day, date back to the twelfth and eleventh centuries. These remains, with surfaces deeply corroded into holes by the effects of oxidation during the lapse of so many centuries, betray their venerable age by the texture of the glass and their warm green tinge. The fragments are unusually thick, five millimetres ($\frac{1}{2}$ inch) being no unusual diameter. The size of the individual panes of this antique window glass, with their original rough edges, is at the most barely twelve centimetres ($4\frac{3}{4}$ inches) in superficial diameter.

The artists on glass in those earlier ages at first had only four kinds of window glass at their disposal, *viz.*, red, blue,

yellow and white (ordinary bottle green), to which were added in the twelfth century green and purple glass. All the glass paintings of this period are characterised by the very sparing use of "black flux," and the colours by a high degree of transparency. However, as may be gathered from the description given, the pictures of that era would be far more correctly denominated mosaics than true paintings on glass.

Finally, in the fifteenth century, glass painting gradually took a fresh turn. The manufacture of glass had made considerable progress; in addition to window glass coloured throughout there were now produced "flushed" glass plates, consisting of plain glass for about three-fourths of their thickness, the remaining fourth being coloured, *i.e.*, blown in two lamellæ direct from the crucible. This glass exhibited numerous advantages for the painter, being clearer and softer in tone; and being shaded with darker tints in places—owing to the running of the molten glass—exhibited a watered appearance, a circumstance utilised by the artist to represent the folding of draperies and garments.

By means of this practice of flashing numerous tints and gradations of all the mixed colours could be obtained, from a pale flesh tint to deep blue violet. The glass painter had also thereby a new means at hand for introducing ornamental details previously unknown in this branch; he could grind out the most delicate decorations in the coloured cover-glass and thereby leave beautiful lustrous patches in the clear glass underneath.

These spaces he painted and shaded with a brownish black palette pigment, and also understood how to apply yellow colour to the reverse of the glass, thus changing the clear silver white of the background to a deep, warm gold.

This second period of the glass-painting industry was also its golden age. "Churches, palaces, town halls, guild halls

and public and private houses were embellished with histories, weapons, emblems and decorations, all in fine colours.”¹

The metallic oxides came into vogue as colouring matters ; the well-known copper scale was mixed with iron scale and used for making the “black flux”. Red was compounded from iron slag, gold-leaf, gum, ruddle and rocaille ; blue from cobalt, or from smalt with an addition of minium, or from zaffre—a mixture of cobalt oxide and sand used for making smalt—with clear glass, saltpetre and minium ; green, as formerly, from copper scale. A beautiful yellow—the so-called “art yellow”—was yielded by the oxides of silver. Respecting the substances capable of colouring glass there were then at disposal a large number of those we now employ for the same purpose. The introduction of these pigments necessitated, by reason of their varied degrees of fusibility, a rearrangement of the qualitative and quantitative composition of the fluxes, as well as, occasionally, modifications in the method of their employment ; and this was particularly the case when the heat requisite to enable the metallic oxide to form with the flux, the chemical compound necessary for the production of a particular tint, was greater than could be employed for firing.

In consequence of these new relations between the proportion of pigment, flux and foundation, the theory of the glass pigments and their fixing media was developed, and has remained almost unaltered down to the present time.

The process and appliances for firing were also considerably improved ; the crude and inconvenient furnace of the first period was now replaced by a more suitable arrangement, a regular furnace with a hearth and ash-pit ; not infrequently we find the furnace already provided with an iron clay-covered cupola, the draught pipe of which concentrated the fire and kept it steady. The iron plate, without

¹ Thomas Garzoni, in his *Allgemeine Schauplatz*, p. 629. Frankfurt, 1641.

sides or cover, on which aforetime the goods were exposed to the fire, was replaced by muffles of baked earthenware or strong sheet iron, which afforded greater protection and ensured the much greater success of the operation of firing. Instead of fixing a definite duration for the firing process, applicable to all classes of work, as formerly, certain indications were recognised as denoting satisfactory progress and the completion of vitrification, whereby the operation acquired a degree of security hitherto but too often lacking.

Finally, the employment of the diamond point, a discovery made in this period, whereby the safe and accurate cutting of glass could be effected, must be mentioned.

The third period of glass painting commenced with the seventeenth century, and this period also witnessed its total decline and extinction. The wars and religious convulsions of that century eradicated the art, the practice of which fell everywhere into desuetude owing to the absence of any demand; and even the art itself, with its empiric technical secrets, was almost totally lost. The last blow was delivered by the extraordinary advance made in the production of progressively clearer and finer plain glass, and of larger panes, especially as a result of the labours of J. Kunkel.¹ A similar state of desolation existed throughout the eighteenth century, the arrangement of colour in the glass paintings of that age being as crude and destitute of taste as the colours of the costumes of the period. The chromatic work undertaken in glass painting was mostly confined to three primary colours: a glaring brownish yellow, an extra deep red and a violet.

The art of encaustic painting on glass (actual painting) was really discovered anew in the nineteenth century. But whereas—as we have seen—the old art of glass painting gradually developed into perfection from its own resources, the new industry exhibited a reversal of this mode by basing

¹ *Ars Vitraria*, 1689.

itself on the developed arts of porcelain and enamel painting, and transferring the technique of the former to a transparent ground—the translucent surface of window glass. In other words the glass painting of the nineteenth century is no daughter of the older art, but an encaustic, petrified offshoot from the art of painting in oils and water-colours, occupying an intermediate position between them in regard to the treatment of colours and mode of application. This closes the history of glass painting.

Painting on earthenware was known to both the ancient Egyptians and Phœnicians, and was subsequently developed by the Arabs and Persians. Independently of these nations the Chinese have produced painted porcelain from time immemorial.

The existing art of decorating earthenware with permanent colours is chiefly due to the French chemists Calvetat and Brongniart, who, by their incessant researches and labours, brought the industry up to a high state of perfection. After the renowned porcelain of Sévres, that of Dresden, Berlin and Meissen is most prized in Germany, on account of its beautiful lustrous and durable colours. The porcelain ware produced in the now defunct porcelain works of Vienna is already of priceless value to collectors by reason of the beauty of the colours employed.

Further particulars of porcelain and enamel painting will be given in the proper chapter, and it only now remains to say a few words about painting on glass and porcelain.

The method of decorating the surface of certain objects made of glass, porcelain, enamel, etc., with such colours as only attain their lustre and adherence by the influence of high temperatures, is called “encaustic painting”. In the case of glass the pigment may be applied partly to colourless, partly to coloured transparent glass (already coloured in the frit stage).

The whole of the pigments employed are metallic oxides or their compounds, a few other substances capable of resisting fire being also used. The rule is that only such colours should be employed as are able to withstand the influence of a high temperature.

Porcelain painting differs considerably from painting on glass, in that, whereas in the latter case vitrifiable metallic colours are employed, which by the action of fire are fused only into the surface on which they are laid and leave the same more or less transparent—in porcelain painting the colours and the porcelain glaze, when fired, fuse and run together, thus permeating the whole of the glaze with colour.

Two chief classes of pigments are differentiated in both glass and porcelain painting, *viz.*, the colouring matter (colouring foundation or the oxide, applied in its original condition by means of an earthy vehicle), and the flux. The latter serves to render the former vitreous, and (being itself of a glassy nature) when fused gives the colours their brilliance and the power of adhering to the surface of the object they decorate.

It is important to remember this difference between colouring matters and fluxes and to keep them separate. According to Gessert the colours requiring fluxes are properly further divided into two classes, *viz.*, glass-painters' fluxes and glass-painters' colours. The latter is the name given to pigments wherein the oxide, in an unaltered condition and merely mixed with the flux, is applied to the glass. By glass-painters' fluxes are meant those compositions in which the oxide and flux have been previously vitrified by fusion before application to the glass. For the sake of clear understanding we will adhere to this classification in the present treatise.

It should also be remarked that chemical combination

does not always result from the fusion of the colouring matter with the flux. For example, in the case of the oxides of iron and chromium the flux is probably merely a vehicle surrounding the colouring matter and attaching it to the object but in no wise contributing to the development of the colour. It is somewhat different in the case of the oxides of copper and cobalt, which produce the colour only through chemical combination with the flux. In this instance it is the silicates and borates of the respective oxides that appear as colouring matters and are employed as pigments.

More extended details will follow in the respective sections of the book: we come now, in the first place, to the objects to be decorated.

CHAPTER I.

THE ARTICLES TO BE PAINTED.

GLASS.

RESPECTING the invention of glass by the Phœnicians little needs to be said, most readers being already acquainted with Pliny's account of the Phœnician mariners who, on the sandy coast near the mouth of the Belus, employed (in the absence of stones to support their cooking pots) some lumps of natural soda they had on board, and found after the fire had been put out that the soda had become fused with sand to form glass. Moreover, Pliny himself ascribed but little probability to this fable, which, for chemical and technical reasons, appears to us altogether incredible. On the other hand the fact remains that the oldest specimens of glass, of which we have any account, originated in Phœnicia and Egypt, and glass blowers are depicted in full work in the reliefs on the royal tombs at Beni Hassan, dating from about 1800 B.C. So much for the history of glass.¹ We will now proceed to make a few remarks on the manufacture of the article, and briefly notice its properties, so far as they relate to our subject.

Glass is divided commercially into four groups according to its chemical composition, *viz.*: 1. Potash or Bohemian crystal glass, perfectly colourless, extremely refractory and hard; 2. Soda-lime glass, also called "French glass,"

¹ This subject is treated of fully by Deville, *Histoire de l'art de la Verrerie*. Paris, 1873.

window glass, bluish green in colour, and somewhat harder than the previous class; 3. Potash-lead glass, crystal glass, soft, fusible, colourless, brilliant, and rings well; 4. Alumina glass, bottle glass, poor in alkali; often contains considerable amounts of manganese and iron, and frequently magnesia in place of potash. It is reddish yellow or dark green in colour.

In preparing glass which, for certain purposes, is more perfect in proportion as it can resist the action of water and chemicals, only just as much potash or soda should be taken as suffices to completely fuse the silica used. On an average three parts of purified potash are reckoned to four parts of quartz sand. Should the glass contain too much potash it is more readily fusible, but has so little power of resisting acid that it is often corroded and eaten right through by concentrated sulphuric acid. Glass made from pure silica and purified carbonate of potash is perfectly colourless and transparent.

The mixture itself, from which the glass is made by fusion, is technically known as the "charge" or "frit". In the present high state of development of the glass-making industry, the greatly improved furnaces and the purer condition of the materials now employed, the fritting is abolished; the glass, with few exceptions, being fused at one operation. Instead of perfectly pure silica (rock-crystal), which cannot be used on a large scale, sand is used, quartz sand being the best, but this must be, as far as is possible, freed from extraneous admixtures, and especially from oxide of iron. Well-known deposits of glass sand occur at Nivelstein (near Aachen—99·97 per cent. silica), Lemgo, Namur, Wight,¹ and in many other places in America and Australia.

Various decolorants ("glass-makers' soaps") are used in making colourless glass, and act in different ways. Thus, for

¹ Isle of Wight.

example, manganese peroxide produces an amethyst tinge by the formation of manganese silicate, but this coloration can be neutralised by the pale green imparted by ferrous silicate, so that the glass appears colourless. Protoxide of nickel is still more serviceable, gradually supplanting the manganese peroxide. Other decolorants are: zinc oxide, antimony oxide, and cobalt oxide. Those mentioned so far act physically by complementing the colour to form white, whereas minium, sodium nitrate, barium nitrate, and arsenious acid decolorise by oxidation.

Respecting the colouring of glass it may be stated that blues are produced by means of cobalt compounds (smalt and cobalt oxide); a clear, perfectly transparent yellow is obtained by uranium, whilst the same metal gives a somewhat turbid yellow coloration in potash glass, with a green shimmer due to fluorescence. Copper oxide colours blue-green, but is mostly used along with chrome oxide, the yellow-green of which it renders bluer. In presence of reducing agents copper oxide is reduced to protoxide which gives a shining, blood-red colour. Silver, although producing very fine pale yellow tints, is but seldom employed for mass colours. For the preparation of white (so-called "alabaster") glass tin oxide is used, and the beautiful "ruby" glass is obtained by means of gold compounds. The oxides of iron, mixed in various proportions, are capable of producing all the glass colours.

Glass must not be regarded as a simple chemical compound, but rather as a variable mixture of certain silicates which remain homogeneous after being fused together and rapidly cooled. When heated, glass gradually passes from the solid to the liquid condition; at about glowing heat it may be bent and drawn out, and at the commencement of red heat may be blown out by a current of air and spun out into the finest fibre. At bright red heat it is inclined to flow

and becomes thenceforward more and more fluid, but even at white heat retains the consistency of a thin syrup. Its behaviour in this respect differs considerably with alterations of composition; whereas silica makes it more refractory, lead oxide produces the opposite effect and boracic acid and fluorine also render it more fusible. When glass is kept for some time at the temperature at which it softens, devitrification sets in, the result being the production of an opaque, crystalline, stony, very hard and but slightly brittle mass. If the interior of a piece of glass be exposed by grinding, etc., it is less able to resist the action of chemical reagents than the natural surface of the glass as produced by heat. Boiling water, when the exposure is prolonged, gradually attacks glass to a greater or less extent.

Glass plates that have been stored for a long time in damp places mostly become coated over with an alkaline liquid, which constantly renews when wiped away; the glass in time loses its lustre and becomes "blind" (opaque); a number of small scales separate from the surface, or the latter becomes covered with a tender, highly iridescent skin.

Blind glass can be made clear again by washing with potash lye or hydrofluoric acid.

This subject is treated more exhaustively in R. Gerner's work on *Glass Making* (*Die Glas-fabrikation*), and W. Merten's *Glass Making and Refining* (*Die Fabrikation und Raffinirung des Glases*).

PORCELAIN.

As far back as the year 442 A.D. porcelain was generally known and used throughout China; but it was only in the fourteenth century that the Portuguese introduced it into Europe. It is supposed to derive its name from them, but so many versions are current of the origin of the word that we prefer not to pin our faith to this one. Many were the

attempts to imitate porcelain, all of which failed until Johann Friedrich Böttger,¹ originally an apothecary's assistant and afterwards a so-called "gold-maker," succeeded by accident. The first successful experiments were made in 1703 with a red clay mass, called red porcelain; but when in 1709 Schnorr, a smith, discovered, also by accident, a deposit of kaolin near Aue (Saxony), Böttger succeeded in producing white porcelain as well. The Government of Saxony did everything possible to keep the process of making porcelain secret, but unsuccessfully, although the factory at Albrechtsburg was treated like a veritable fortress and the drawbridge let down only by night. The secret of the manufacture spread with a rapidity surprising for that age. For instance, a porcelain factory was set up in Vienna in 1710, and in the following year white porcelain was offered for sale at the Leipzig fair; works were started in 1756 at Berlin; in 1757 at Drankenthal; in 1758 in Thuringia, and shortly afterwards in Bohemia.

Porcelain is extremely hard, with a fine, dull fracture; is translucent in thin layers, and withstands rapid changes of temperature, especially when unglazed. The glaze is so intimately incorporated with the mass that no border line between them can be detected. The characteristic of porcelain is that it consists of a substance which, at the highest attainable furnace temperatures, fuses and envelops the extremely fine particles of infusible porcelain earth. The chief constituent of porcelain is the so-called porcelain earth (kaolin), a pure clay (composed solely of alumina and silica, mostly resulting from the weathering of felspar) which contains no—or but very little—lime, and is infusible at the fiercest furnace heat. Kaolin or porcelain earth differs in physical properties from ordinary clay mainly in its inability

¹ Born in Schleiz (Voigtland) in 1682 and died at the age of thirty-five years.

to retain water and form a plastic, tough paste. In its natural, unwashed condition, kaolin falls apart in water to a fine powder like fuller's earth.

After the kaolin has been broken down by passing it between rollers, and well washed, mixed with silica, quartz or sand, and gypsum or felspar, and also roasted, calcined, ground and sifted, the materials are made into a thin gruel with water and mixed with the powder obtained by grinding fragments of white porcelain, the whole being then intimately mixed and ground, kneaded, cut up and kneaded over again. The manufacture of the ware on the wheel or in moulds, by pressing or beating, is then proceeded with, the outline being made sharper, after drying, by tooling in the lathe and polishing by means of small plates of horn and ivory. Hollow, human or animal figures are pressed into separate moulds for the two halves (lengthwise) of the figure, the halves being joined after removal from the moulds, and the traces of the junction obliterated and smoothed down.

The air-dried ware is enclosed, for protection from smoke and soot, in refractory capsules, in which it is supported at the bottom and sides by colombines and pernettes to prevent it from setting crooked or sticking in the baking, and is fired in a kiln made of fire-brick, frequently cylindrical in shape, and divided either longitudinally or transversely into three sections. When the capsules with the contained ware are properly inserted, and the fire gradually raised to a maximum, the progress of the firing is observed by taking out test-pots which are examined in the light outside the kiln. Only when the kiln has been suitably cooled down, a process requiring several days, are the capsules containing the ware taken out. In this condition the porcelain is termed "biscuit". Now comes the glazing. The glaze is prepared from the same materials as the porcelain itself, only that it is rendered more fusible by the employment of a larger

proportion of gypsum, felspar or porcelain sherds. Again enclosed in capsules and placed in the kiln, the glaze is fused on to the ware, test-pots being also used in this case to enable the completion of the operation to be determined. The ware on removal from the cooled kiln is classified into fine, medium, outshots (defective but still usable) and "wasters" (unusable and destined to be broken up again).

A good deal of ware comes out of the kiln possessed of various defects which may be remedied by placing the thicker articles in a hotter situation and the thinner articles in less highly heated positions, or by employing various fusible or refractory mixtures, the former for thick and the latter for thin goods.

In firing the ware decreases in size by about one-seventh in circumference, so that this shrinkage must be taken into consideration in making articles intended to have a definite size when finished.

ENAMEL.

It is difficult to define strictly the difference between enamel and glass. Under the former term is, however, understood a fusible opaque or transparent glass flux (often coloured by means of metallic oxides), which is mostly employed for coating metallic objects. In the case of transparent enamels all the constituents are completely fused, whereas opaque enamel is rendered so by the milky turbidity resulting from the admixture of bodies that are not readily fusible (chiefly oxide of tin).

Enamel is employed for two separate purposes, one being the decoration of "articles de luxe" and the other the production of a protective covering to metallic appliances for domestic or technical use. We are only concerned with the former.

B. Bucher of Vienna describes the enamelling of metallic

objects as follows: "The chief component of the majority of enamels is a glass rendered fusible by a large admixture of lead oxide and occasionally by borax or some other flux, so that, without becoming too thinly fluid, it forms a smooth surface at a moderate red heat. In enamelling the mass should not actually become perfectly fluid but should assume a pasty consistency, so that the enamel powder on the surface of the metal unites to form a cohesive covering which, on cooling, will look as though it had really been liquefied. When a metallic surface is to be only partly coated with enamel a boundary is formed by soldering metal wire or by depressing the surface in any convenient manner for the reception of the enamel (*cloisonné* enamelling). In order to facilitate the adherence of the enamel to the metal the surface of the latter is often covered by a network of cross-hatchings or worked up as rough as possible. The metal is then boiled in potash lye, rinsed with weak acid, washed with water and covered with a thick layer of moist enamel previously ground to a granular powder. It is then dried in the air, heated over glowing coal until the evolution of fumes ceases, and then, without being cooled, transferred to the strongly heated muffle of the enamelling furnace. As soon as the enamel is evenly fused the article is carefully (so that it can only cool slowly) removed from the muffle and washed with very dilute nitric acid and cold water, after which it is covered with a fresh layer of enamel powder and again fused. When the third coating has been affixed in the same way, the surface—particularly when large and flat—is rubbed over with wet sandstone and the article returned to the furnace in order to produce the requisite smoothness. The surface may then be painted, and when this is dry the colour is fixed by a final firing in the muffle.

Now-a-days almost any colour can be imparted to the enamel mass. White—and thereby always opaque—enamel

is obtained by using oxide of tin, and if other colours are mixed with white enamel the opacity remains. Blue is produced by cobalt oxide; white enamel gives with this oxide forget-me-not blue. The various yellow colours are produced by silver chloride, lead antimoniate and zinc oxide, or by zincite, antimony oxide and specular iron ore, or by ferric oxide or uranium oxide. Green is obtained by chromic oxide or cupric oxide, nickel oxide, copper antimoniate, or cobalt antimoniate.

The finest red colours are obtained by means of gold purple, whereas cuprous oxide, ferric oxide or silver sulphide will produce a cheaper but less handsome red. Manganese oxide gives violet; the same oxide, with chromic or ferric oxide, brown; and a mixture of violet, dark blue and green produces black. The intensity of each colour naturally depends on the amount of colouring matter employed, and the most diversified tints can be prepared by altering the proportions of the mixtures. Fuller information on the preparation and use of enamel for artistic and technical purposes will be found in P. Randau's work on the subject (*Die Fabrikation der Emaille und das Emailiren*, 2nd edition).

STONEWARE.

Stoneware is not very often painted, and in the description of this material we will therefore confine ourselves to the most important particulars.

This ware was invented by Josiah Wedgwood about the middle of the eighteenth century. It is a hard, dense material (so much so that fire may be struck from it), and can endure remarkable alterations of temperature without cracking. It is prepared from white clay (or rather from clay that burns white) and ground flint-stones intimately mixed together and fired—not merely burned hard, but caused to

sinter (commencing to fuse) by intense heat—on which account it exhibits a clean glassy fracture. Stoneware is made of various colours, chiefly white, yellow and black; and blue or green ware is not infrequently met with. The unglazed stoneware, with a dull alabaster-like surface, is termed biscuit.

Moulding and firing are performed in the same manner as for porcelain, and the method of painting and firing the colours is also the same.

FAIENCE.

This class of ware is named after Faenza in Italy, whence it was for a long time obtained, and is made of a finer washed clay than that used for ordinary earthenware. Clay that will burn white or yellowish in colour is selected, and faience pottery is prepared with great care and accuracy, with a very lustrous glaze, and is generally decorated with fine paintings, or with pictures applied by the “transfer” process.

The washed clay is mixed with sand or powdered alabaster in the proportions ascertained as most suitable by experimental firing, and prepared in the best possible manner by treading, kneading, scraping, etc.; and is then made up into ware on the wheel or by moulding. Goods made on the wheel are, however, when air-dried, tooled again in a lathe to ensure greater accuracy, and then fired in a faience kiln, which is generally divided into three superimposed sections, communicating with each other by perforated partitions. In the two upper divisions the pottery is fired, the lower serving as the furnace. The ware is enclosed for firing in refractory fire-clay cassettes or capsules, and is first half-finished without glaze. A coating of the latter is then applied by dipping the ware into the finely ground glaze stirred up in water, and fired until complete, the progress of

the operation being watched by taking sample pots through suitable apertures in the kiln, in order to see whether the goods are properly fired and the glaze well fused. After cooling down, follows painting (see porcelain painting), or printing with pictures.

Those interested in the decoration of porcelain or other earthenware with pigments, require to study the special properties of the various classes of ceramic ware, and are advised to refer to Ludwig Wipplinger's work on ceramics (*Die Keramik*).

CHAPTER II.

PIGMENTS.

THE pigments employed for painting on glass and earthenware may be grouped in three classes :—

1. Metallic oxides and salts.
2. Earths or earthy bodies.
3. Metals.

The metallic oxides and salts are the actual vitrifiable pigments, whereas the earths (ochre—*Terra di Sienna*) are either coloured by metallic oxides or are white; they are generally termed “coaters,” since they are opaque and do not assume a glassy appearance until covered by a coating of glaze. The metals are only used in the metallic condition—and in an extremely fine state of division—for metallic decorations or lustre.

I. METALLIC PIGMENTS.

The coloration of glass masses and earthenware is mostly effected by means of metallic oxides which are either previously fused, or simply mixed, with soft fusible glass—the flux or binding material. The fluxes are soft fusible glasses which become fluid at moderate temperatures and cause the colouring matter, pigment, or oxide to adhere to and combine with the glass.

ANTIMONY OXIDE.

The pigment employed under this name in glass painting is altogether wrongly designated, since it is really the bi-

(acid) antimoniate of potash. Metallic antimony is the fundamental substance employed in the production of this preparation. It is tin-white in colour, very lustrous, and exhibits a radially laminated structure; is hard, but very brittle, and easily reduced to fine powder. The specific gravity is 6.702-6.860; it glows and fuses at 700° C., and sublimes when raised to white heat in closed vessels.

If metallic antimony be calcined along with six parts of saltpetre, and the mass maintained at strong red heat for some time, the acid antimoniate of potash—our wrongly named antimony oxide—is produced. The product is powdered and extracted several times with cold water (in order to remove the wholly or partly decomposed saltpetre); the resulting white powder is then boiled with water for an hour and the solution filtered. It does not become turbid when cooled.

The insoluble residue is impure biantimoniate of potash, and must be re-washed with boiling water. On the other hand the solution contains only potassium antimoniate, which, however, can be converted into the pure acid salt by passing a current of carbonic acid gas through the liquid. The resulting salt forms a white powder, insoluble in water.

This substance cannot by itself be used for the production of a yellow pigment, but when mixed with zinc oxide and ferric oxide in suitable proportions it gives very fine yellows, from the palest sulphur to reddish orange tints. The latter shade is, however, obtained more effectively with lead chromate or uranium oxide.

NAPLES YELLOW.

Many glass painters replace antimony oxide, for certain purposes, by commercial Naples yellow (lead antimoniate), which can be ground along with the flux and used

direct. The commercial substance is, however, not always of constant composition, the quantitative ratio of its components varying to such an extent that its employment should be decidedly discountenanced. Some Naples yellow will fuse at red heat, whilst others require three times the quantity of lead flux before being usable. Since certain definite shades of colour are required, it is evident that the necessary testing of the fusibility of this substance causes considerable loss of time.

One part of antimony oxide and three parts of purified lead oxide or minium will give a very fine pale yellow; the first named used alone produces a yellowish white. In Brunner's method one part of perfectly pure tartar emetic is mixed very intimately (by grinding together) with two parts of lead nitrate and four parts of common salt, the mixture fused in a Hessian crucible at a moderate red heat, and the fluid mass poured on to a cold iron plate. When cold the mass is extracted with boiling water, which leaves the lead antimoniate behind as a more or less dark yellow powder.

It is, however, not at all an easy matter to attain this favourable result with certainty in all cases. If a certain degree of heat be exceeded, though merely by a little, a hard, solid mass results, which cannot be brought to fine powder by boiling ever so long, but remains as a granular mass of inferior brightness of colour.

Even when the operation succeeds, the shade of the colour often varies, so that at one time a sulphur yellow and at another an orange yellow product is obtained. As a rule, it may be assumed that with lower temperatures the products will be lighter in colour, and darker (with a red tinge, so that they may be classified as orange) when greater heat has been used.

According to another recipe, the mixture consists of two parts of tartar emetic, four parts of lead nitrate and eight

parts of common salt. If the fused mass be treated for a long while with very dilute hydrochloric acid, a certain amount of lead oxide is removed, whereby a product of greater brilliancy is obtained. Great care is, however, necessary in carrying out the hydrochloric acid treatment, since, by the use of acid that is too strong, the whole product can easily be rendered valueless for the purpose in view.

Naples yellow may be prepared, by the so-called Parisian method, as follows: Metallic antimony is oxidised by fusing in air, and to each twelve parts of antimony are taken eight parts of minium and four parts of tin oxide, and the whole fused together at a moderate red heat.

BARIUM CHROMATE.

Barium chromate is not often employed. Its chief uses are for porcelain and faience painting, and it gives very fine yellow colours. The preparation is not now met with in commerce, but is not difficult to make. To this end barium chloride is prepared by dissolving natural barium carbonate (Witherite) in hydrochloric acid to a saturated solution, which is filtered and slowly evaporated at a moderate heat, whereupon octahedral tabular crystals separate out and are from time to time freed from the mother liquor by pressure.

An aqueous solution is made of this salt, and, if acid, is neutralised by the addition of sodium carbonate until a precipitate commences to form. A solution of neutral (yellow) potassium chromate is added so long as any precipitate comes down, and the latter is then washed and dried.

The resulting preparation is a canary yellow salt insoluble in water, but completely soluble in nitric acid. It contains 59.88 per cent. of barium, and 40.12 per cent. of chromic acid.

LEAD CHROMATE.

Lead chromate, commercially known as "chrome yellow," does not generally consist of pure chromium oxide or lead chromate, but mostly contains admixtures of lead sulphate, lead chloride, or gypsum (sulphate of lime), added to tone down the colour, although the fusion of the compound is thereby rendered more difficult.

Even if the preparation is obtained in a pure state the variable composition of the different commercial grades is too great to allow the article to be used with any degree of security.

The renowned former director of the Sèvres' porcelain works, A. Brongniart, gives the subjoined analyses of several commercial chrome yellows:—

ANALYSES.

Chrome Yellow.	Pale.	Deep.	Orange.	Cologne Yellow.
Lead chromate	17·10	20·17	19·01	24·50
Calcium sulphate	70·01	58·45	61·02	60·00
Lead sulphate	1·99	21·08	4·71	15·40
Barium sulphate	10·00	—	15·16	—
Loss	0·90	0·30	0·10	0·10
Total	100·00	100·00	100·00	100·00

It is therefore advisable to prepare lead chromate for painting on glass, porcelain, etc., oneself. The chief essential is to use pure raw materials, taking special care to have the potassium chromate free from potassium sulphate, since otherwise lead sulphate would be precipitated.

The readiest mode of preparation is as follows: A solution of sugar of lead (lead acetate) in water, to which is added a little acetic acid, is added to a solution of red potassium chromate, so long as a precipitate continues to fall. The deposit is then washed five or six times with fresh water and dried.

The lead chromate comes down as a beautiful dark yellow powder ; neutral (yellow) potassium chromate gives an orange yellow, whilst acid (red) potassium chromate gives a yellowish red or dark red precipitate.

Some people assert that chrome yellow requires to be fused before being employed as a pigment, but this is altogether superfluous.

In order to produce the finest chrome yellow, which shall leave nothing to be desired in point of beauty of tint, the following method should be adopted: Lead acetate is dissolved in water, and the solution diluted with an equal volume of water ; then mixed with vigorous stirring with a similarly diluted solution of neutral or acid potassium chromate. The precipitate immediately produced rapidly subsides on account of its great weight, and must be washed with pure water as long as any soluble matter is taken up, and is then spread on cloths and dried in the air.

The finest product is obtained by working with the following proportions :—

Lead acetate solution	-	-	-	100
Potassium chromate solution	-	-	-	50 (red bichromate), or
„	„	„	-	40 (yellow „).

SILVER CHLORIDE.

Although silver chloride is frequently used in glass painting for the production of fine, transparent yellows, it is less extensively employed in painting on porcelain, and that only for purple and carmine—not for any other colour.

Silver chloride is prepared as follows: Pure metallic silver is dissolved in nitric acid by the aid of warmth. In order to avoid having an excess of acid, rolled silver is added to the acid until no more is dissolved, *i.e.*, the solution is saturated. The succeeding operations are best carried on in

a dark room to prevent the silver turning black. The silver nitrate solution, after being suitably diluted with water, is well shaken up and placed in a large glass flask, and to it is added hydrochloric acid until precipitation ceases. After a few hours' rest the water is decanted from the precipitate into another flask in order to give the silver salt, still in suspension, time to subside. The curdy precipitate in the first flask is washed five or six times with fresh, clean water; the washing to be continued so long as a white precipitate (indicative of hydrochloric acid) is produced on the addition of silver nitrate to the washings, or a red brown precipitate (copper ferricyanide) with potassium ferricyanide.¹

When the water ceases to become turbid the silver chloride is dried by being enclosed in doubled dark blotting paper and dried on a flat plate in a warm oven; when dry it is stored in black glass bottles. If this precaution be neglected, the silver chloride will turn black under the influence of light, and it will be impossible to obtain perfectly pure yellow or fine carmine and purple therefrom.

Silver nitrate (so-called *lapis infernalis*) being now obtainable in a very pure state commercially, it is better to employ this preparation when making silver chloride.

The nitrate is dissolved in distilled water and dilute hydrochloric acid is added (by artificial light) so long as a precipitate forms; the latter is then repeatedly washed with water and finally dried in the dark.

Silver chloride is an insoluble white powder, at first caseous and bulky, but on settling collects to a heavy snow-white mass; it is soluble in hydrochloric acid, particularly in concentrated acid, so that an excess of hydrochloric acid

¹ Copper, even though in small quantities, in the silver chloride exerts a highly prejudicial influence on the colours, and also contaminates them. It is also strongly advisable to employ distilled water in order to avoid the introduction of lime into the preparation.

must be avoided in precipitating. When heated, silver chloride first turns rose red, then fuses to yellow, but turns to white on cooling, and when cold may be cut like horn, from which circumstance it is known as horn silver. The percentage composition is : Chlorine 24·67, silver 75·33.

CHROMIC OXIDE.

Chromium (from *χρῶμα*, colour), so called from the property inherent in its oxides of forming pigmentary compounds, was discovered, almost simultaneously, by Vauquelin and Klaproth in the year 1793, and was first prepared from red Siberian cerussite. The metal is whitish grey, fairly lustrous and of medium granular structure, very brittle and breaking under the lightest blow.

Chromic oxide forms an important constituent of chrome iron ore. The pure oxide is of a fine dark grey colour, the shade being, however, dependent on the method of preparation. The oxide, heated to bright redness, is crystalline and very dark coloured, and in this condition is impervious to the action of acids, but alkali in a state of fusion converts it into alkali chromate, especially in presence of saltpetre. The various methods of preparing this are subjoined :—

1. *Potassium Bichromate and Sulphur Method.*

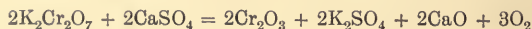
The cheapest way to produce chromic oxide is by heating potassium bichromate and sulphur to redness, extracting the mass with very dilute sulphuric acid and washing the residue. The sulphur reduces the chromic acid; sulphur dioxide is evolved on the application of sulphuric acid to the hot mass, and the sulphide and sulphate of potassium pass into solution, leaving pure chromic oxide behind. The larger the amount of sulphur employed the paler will be the colour of the resulting product. The purity of the potassium bi-

chromate used exerts particular influence on the fineness of colour of the chromic oxide produced by this method. Should the former contain iron in quantity the product will always be off-coloured and never of fine quality.

It is advisable to take nineteen parts of potassium bichromate and four parts of sulphur; these will produce 9.33 parts of chromic oxide. If no bichromate free from iron can be had, the colour of the product can be somewhat improved by treatment with dilute hydrochloric acid, wherein ferric oxide is more readily soluble than chromic oxide, the latter being—especially when heated to redness—soluble only with difficulty.

There are many prescriptions given for the preparation of chromic oxide by the aid of sulphur, but in all of them the above-mentioned rule applies: the more sulphur used the paler the product obtained.

According to A. Casali, a chrome green, fulfilling all requirements, may be prepared by heating to bright redness a mixture of one part of potassium bichromate and three parts of calcined gypsum, the mass being subsequently extracted by boiling with very dilute hydrochloric acid. The reaction is expressed by the following equation:—



The lime is dissolved by boiling with hydrochloric acid, and when, after prolonged boiling, the liquid exhibits a decided acid reaction, it is poured off and the residual chromic oxide washed with hot water and dried.

The potassium bichromate should be finely powdered and mixed with one half its weight of powdered sulphur. This mixture is placed in crucibles or capsules, and heated to pale red heat in a blast furnace. The spongy green mass remaining in the crucible when cold consists of chromic oxide mixed with potassium sulphate, which latter must be re-

moved—a tedious operation owing to the sparing solubility of this salt in water. It may be effected much quicker by the addition of a little sulphuric or hydrochloric acid. When completely purified the pigment is filtered on linen filters and dried on boards. One hundred parts of potassium bichromate and fifty parts of sulphur will yield about sixty-eight parts of chromic oxide, provided the pure salt has been used; should it, however, as occasionally happens, contain a deal of potassium sulphate the result will not be so good.

Brongniart recommends a proportion of one part of potassium bichromate and two of sulphur, but this always results in the production of a larger amount of sulphate, and concurrently sulphide, of potassium. The resulting chromic oxide must, for the purposes of the glass and porcelain painting industry, be re-heated to redness, whereby the oxide on attaining a certain temperature parts with its water and immediately—in a few seconds—takes fire, whereupon the temperature again falls, without any loss being occasioned.

2. *Ammonium Chromate Method.*

The chromate is heated very gradually, and when a certain temperature is attained the salt glows and immediately changes into a dark-green, almost black, mass, very similar in appearance to rolled-up tea leaves. This, when extracted and ground, yields a fine green, the quality being in inverse ratio to the temperature employed for decomposition.

3. *Wet Method.*

Chromic oxide may be prepared in the wet way, but the product cannot be compared in point of fineness of colour with that from dry methods. When a solution of chrome alum is mixed with a solution of soda a grey-green pre-

precipitate of hydrated oxide is formed, which, when washed and heated to redness, leaves pure chromic oxide behind.

In a similar fashion chromic oxide may be obtained by mixing potassium bichromate solution with hydrochloric acid and continuing to add small quantities of alcohol so long as any reaction results and the green colour of the liquid progressively deepens. A solution of chromium chloride is produced from which the hydrated oxide may be thrown down by soda as before.

According to Brongniart this gelatinous precipitate can be advantageously employed in the unroasted condition for the production of the bluish-green pigments obtained by mixing chromic oxide and cobalt oxide. The moist hydrated oxide is mixed on a glass plate with moist cobalt oxide and then dried and strongly heated. Very fine, pure bluish-green colours are thus obtained, the shade varying with the proportion of cobalt oxide employed.

4. *Mercurous Nitrate and Potassium Chromate Method.*

A very fine chromic oxide can be prepared by this method, but it should be remarked that the process is rather expensive and not unattended with danger.

In the first place mercurous nitrate is prepared by diluting pure nitric acid with three to four times its weight of water and immersing mercury in the mixture. Solution goes on gradually and is attended with effervescence, which subsequently decreases as the greater part of the free acid becomes saturated with mercurous oxide. Pointed needles then begin to form in the liquid and may be separated by pouring off from the undissolved mercury and dried by very moderate warming. The crystals consist of—

Mercurous oxide -	-	-	-	-	74.29
Nitric acid -	-	-	-	-	19.29
Water	-	-	-	-	6.42
					100.00

The mercurous nitrate is now dissolved in water to which has been added a little nitric acid in order to prevent the decomposition of the oxide to a basic or acid salt, and an addition of successive portions of a dilute solution of potassium chromate is then made. The resulting red, flocculent precipitate is purified by a large quantity of water, then dried and finally calcined in a crucible, whereby the mercury is volatilised and the chromic acid reduced to chromic oxide which possesses a delicate green shade of colour.

The chief condition necessary for the success of the preparation is the careful washing of the precipitate with boiling water until the washings run off quite pure.

Excess of mercurous nitrate should always be avoided, since it greatly increases the cost without improving the colour. The best effect is obtained when the potassium bichromate is in excess. Delong demonstrates that the bichromate in excess exerts a favourable influence on the colour by increasing the fineness of division of the chromic oxide.¹

Another method of preparation is by heating a mixture of potassium bichromate and ammonium chloride (sal ammoniac) and extracting the mass with water.

According to Jean² the waste chrome alum from the aniline green and aniline violet works is now used for preparing chromic oxide. To this end one part of chrome alum is strongly calcined with three parts of carbon; sulphurous acid is evolved and a mixture of potassium sulphate and chromic oxide remains behind, and can be separated by means of water.

¹ It is worthy of note that silica freshly precipitated from water-glass solution forms, when mixed with chromic acid, a rose-red compound, insoluble in water and undergoing no change at the temperature of the porcelain kiln.

² *Comptes rendus*, vol. lxviii., p. 198.

Chromic oxide has an extraordinary power of withstanding heat, and can therefore be employed both in glass and porcelain painting for entire groundworks.

A fine, brilliant chrome green cannot be prepared with certainty unless the potassium bichromate be quite free from iron. Even a very small proportion of this body in the salt exerts an unfavourable action on the brilliancy of the colour. Direct experiments have shown that the bichromate may be freed from iron by recrystallisation, without any particular difficulty. The best way to effect this is by making a saturated solution of bichromate in boiling water, and, after filtering boiling hot, cooling down the solution as quickly as possible, with continual stirring. The fine crystalline meal thus obtained is placed in a funnel and left until all the liquid has drained off, and is then rinsed with a little cold water to drive out the mother liquor. By this simple operation an extremely pure salt is obtained and will yield a fine shade of chrome green.

IRON OXIDE (FERRIC OXIDE).

Ferric oxide occurs in nature as red ironstone (hæmatite), specular iron ore, brown hæmatite, martite and glimmer, as well as in small quantities in many other minerals which frequently owe their colour to this oxide. It occurs in many varieties of hæmatite forming a valuable iron ore; the specific gravity of the pure natural ferric oxide varies between 5.19 and 5.23. The natural oxides are not, however, suitable for direct employment for painting; their composition is, for the most part, very variable, and, as their fusibility corresponds, they are unsuitable for use.

Pure ferric oxide may be prepared artificially as an amorphous red powder, by calcining the hydrated oxide or

the oxalate of iron; by heating anhydrous ferrous sulphate with common salt, or the amorphous oxide with ammonium chloride and extracting the residue with water, it remains behind as black (frequently magnetic) scales which, when reduced in a current of hydrogen, yield the metal in the same form. When ferrous or ferric sulphate is strongly calcined a residue is left consisting chiefly of ferric oxide, but also containing appreciable traces of sulphuric acid. This is the chief constituent of the well-known "*caput mortuum*".

No other preparation yields so many shades of colour as ferric oxide, since it produces orange red, blood red, flesh red, carmine red, lake red, violet red, brown red, red brown and black, and that, too, from the pure oxide alone, the modifications being entirely dependent on the stronger or fainter, longer or shorter action of fire. It is manifest that no ordinary care and skill are requisite to hit upon the correct method of producing each shade exact to standard. Moreover, the shade may be affected in the highest degree by the quality and suitability of the preparation itself, as also by the use of a warm or cold concentrated or dilute solution and by the means employed for solution and precipitation.

Although ferric oxide may be used in all instances for glass painting, and is frequently employed for yellow, red, brown and black colours in equal proportion, this is not the case in porcelain, faience and stoneware painting. The preparation is also used here for the same colours but can only endure the same heat as the muffle colours, whereas in the high temperature of the porcelain kiln the colour would be entirely or partly destroyed, since ferric oxide combines with the silica of the felspar to form the almost colourless compound ferrous silicate.

There are two methods of preparing ferric oxide for glass and earthenware painting, differing according to the object in view; for all colours except red the ferric oxide from com-

mercial ferrous sulphate is used, but for the latter colour it is better to prepare the iron salt oneself.

1. *Preparation of Ferric Oxide from Ferrous Sulphate.*

The oxide for yellow-brown colours for glass painting is prepared as follows : Pure ferrous sulphate (green vitriol) is dissolved in hot water and poured into a porcelain evaporating basin, which is then covered with a thin cloth to keep out dust, dirt, etc. After fifteen to twenty days, during which time the liquid has been stirred twice a day with a glass rod, the water is poured off and the residue used. This latter actually consists of basic ferric sulphate, the name "ferric oxide" being therefore only a technical term.

Another way of preparing ferric oxide is by dissolving two parts of pure ferrous sulphate in five parts of distilled water in a porcelain basin, and, when solution is complete, adding thereto three parts of iron filings previously cleansed by hot water. The whole is left to stand for four hours, with intervals of stirring ; then filtered through paper and transferred to a perfectly clean iron pan, where it is evaporated over a slow fire down to about one quarter its original volume. The whole is then placed in a crystallising basin and stored in a cool place. The liquid, originally very turbid, becomes paler in colour after a few days, and finally crystals are formed which are removed and dried on blotting-paper. They are then carefully calcined and finely ground, and lastly heated to redness in a wide pan which is set in the fire and kept there until the powder has been exposed to a dark, brown-red heat for a quarter of an hour, the powder having been kept stirred with a spatula. (The operator must take care to protect himself from inhaling the acid vapours.) To ascertain if the operation has succeeded, a little of the powder is taken out of the crucible and thrown

into a porcelain basin, the bottom of which is moistened with cold water; should the powder show a yellow coloration the preparation is only half converted into oxide, but if it produces a fine red, without any tinge of yellow, then the process is complete. This heating is the most difficult part of the operation, for whereas, on the one hand, an insufficiently-roasted preparation will never produce a fine colour and quite one-half will be wasted in lixiviation, on the other hand over-roasting results in very dark and dull colours.

Ferric oxide may also be prepared by using ferric sulphate and potassium sulphate, the procedure being as above, except that the precipitate must be heated to redness immediately; the method is, however, not recommended.

Ferric oxide for black can be simply prepared as follows: Pure ferrous sulphate is finely crushed and exposed for between fourteen days and three weeks to the heat of the sun in summer or stove in winter. The water of crystallisation thus evaporates spontaneously and the residual powder can be at once placed in a crucible and exposed to a red heat. After cooling, the product is ground to a pasty mass with old olive oil and again heated to redness, whereupon the mixture quickly takes fire, the oil burns away and a deep black powder is left, which is ground down fine in water and stored for use. Should the powder not attain perfect blackness, the above operation with olive oil and burning is repeated.

The occasion is suitable for a few remarks on ferrous sulphate itself. This substance is rarely met with in a pure state in commerce, the ordinary impurities present being magnesium sulphate, manganous oxide and zinc oxide. As these impurities cannot be detected by external appearances, it becomes essential to determine at any rate the amount of ferrous sulphate in the substance, the impurities having mostly a secondary influence only. To determine the con-

tent of iron fairly accurately, without much trouble, Gentile advises weighing twenty-five grams of the sulphate into a tared porcelain basin, which is then warmed slowly over a gas or spirit flame to drive off the water and afterwards kept at a good red heat for about half an hour. The ferrous sulphate is thereby decomposed into sulphuric and sulphurous acids, which are evolved, and ferric oxide, which remains behind in the crucible. Should the residue weigh more than seven and a half grams, it may confidently be assumed that it is impure, and that in addition to ferric oxide there are present sulphates (such as those of the metals referred to above) undecomposable at the temperature employed. The red mass is then moistened, filtered through a tared filter, washed, dried and weighed as red ferric oxide. Thirty-nine parts are the exact equivalent of 138 parts of ferrous sulphate, and the percentage of pure ferrous sulphate in the original substance can easily be calculated. For instance, if the residue weighs 25 the amount was $39 : 138 = 25 : x$, $x = 88.5$ per cent.

Good ferrous sulphate is pale green, bluish green—not yellow green—in appearance, and is readily soluble both in cold and hot water.

2. *Ferric Oxide for Fine (Red) Colours.*

It is advisable to prepare the ferrous sulphate for colour-making oneself, and have it perfectly pure. To this end a few kilograms of ordinary shoe nails, which are made of very pure iron, are placed in a large bottle and suffused with dilute sulphuric acid (one part acid to ten parts water), small additions of acid being made from time to time until merely a small residue of iron remains undissolved. The solution is filtered and evaporated down at moderate heat, to about one-quarter the original volume, in a porcelain basin containing a

few more nails. On cooling, crystals of pure ferrous sulphate will separate out, and, the liquid (which on further concentration will yield another crop of crystals) being poured off, may be dried on bricks and stored in properly closed glass receptacles.

The preparation so obtained is employed for the production of ferric oxide by being crushed and slowly calcined by exposure to moderate warmth for a long time, so that the crystals do not melt. When all the water of crystallisation has passed off, the residual white mass is ground to very fine powder; the finer the powder the better the result. This powder is now spread out regularly, and not too thickly, over the bottom of a wide, flat porcelain capsule, and then heated to redness in a muffle as slowly as possible. The colour assumed by the oxide must be scanned very closely, and when the desired shade is attained the fire is drawn and the muffle allowed to cool down gradually. The testing of the colour is effected by taking small samples from the muffle at short intervals by means of an iron spatula.

When the ferric oxide is thoroughly cooled down it is washed several times with boiling water and dried. During calcination the oxide becomes first reddish yellow, then redder and redder, the yellow tinge disappearing progressively, until at last the colour is violet red.

A very useful ferric oxide pigment may be produced in the following manner: A solution of seventeen parts of sodium carbonate in sixty-eight parts of water is prepared and raised to boiling in an iron pan, and stirred whilst ten parts of crystallised ferrous sulphate are added, a little at a time. The boiling and stirring are continued until the ferrous sulphate is completely dissolved, and the resulting greenish-white precipitate is then left to subside. This precipitate, consisting of ferrous carbonate, is washed several times with water and then spread out in thin layers exposed

to the air. Already, during the washing process, the precipitate will have begun to turn yellow, and after a very short time in the air will become converted into ochre (ferric hydrate).

The product, when dried and heated to redness, yields a fine red powder of pure ferric oxide, the shade of which is, however, dependent on the roasting temperature employed. The higher this is carried and the more the operation is prolonged, the darker, as a rule, will the resulting product be.

3. *Vogel's Iron Red.*

This preparation, which is distinguished by its peculiar brilliancy, and is, therefore, highly suitable for a painter's colour, is produced by heating a solution of ferrous sulphate to boiling and then adding a saturated solution of oxalic acid. A greenish yellow precipitate of ferrous oxalate is formed, which, after being collected on a filter, is well washed with water. After drying, the precipitate is placed in a flat iron basin and heated to a temperate of about 200° C., whereupon it decomposes and is converted into a particularly soft powder of bright red colour, consisting of pure ferric oxide. From this powder the various shades of colour can be prepared by exposure to red heat in covered crucibles.

Many esteemed glass painters and technical men have upheld the opinion that the substitution of organic acids in place of inorganic acids for dissolving the iron in the preparation of ferric oxide would facilitate the production of the most extensive variety of shades of red oxide, but this view is erroneous.

FERROUS CHROMATE.

The substance often employed under this name, in the glass and porcelain painting industry, for the preparation of fine brown colours, owes its designation to its discoverer,

Brongniart; the production of actual ferrous chromate is impossible, owing to the immediate reduction of the acid to chromium oxide, and our preparation is nothing but a compound of chromic oxide and iron ($\text{Cr}_2 \text{O}_3$, Fe O), which occurs in nature in dense, black, heavy masses—and occasionally in the form of octahedral crystals—as chrome iron-stone.

The method of preparation is exceedingly simple. Potassium chromate is dissolved in distilled water, diluted with thrice the volume of similar water and then left to stand, care being taken to prevent access of dust. Meanwhile a similar solution of pure ferrous sulphate is prepared, and on the two solutions being united a precipitate is produced, which, after five or six careful washings, is dried, heated to redness and finally ground on removal from the cold crucible.

GOLD PURPLE.

Among the metals precipitating gold from solution,¹ tin exerts the most notable action, in that the precipitate is of a purple colour, and is therefore called gold purple. If a rod or leaf of tin be inserted in a solution of gold a sedimental purple cloud immediately forms around it. When metallic tin is used the precipitate is more inclined to brown, the colour being finer if a solution of tin in hydrochloric or nitrous hydrochloric acid is employed. This purple precipitate is a compound of tin oxide with the protoxide of gold in the proportion (according to Berzelius) of 28·2 per cent. of gold to 64 of tin oxide. The tin, or protoxide of tin in the solution, continues to deprive the gold of oxygen and itself becomes peroxide of tin, whilst the gold is reduced to a lower stage of

¹ Gold, as is well known, is only soluble in aqua regia—a mixture of nitric and hydrochloric acids. Further particulars follow.

oxidation, and both come down in a condition in which they are insoluble in the acids present.

Several conditions are essential to the production of a fine gold purple. The gold solution must be free from nitric acid, since this acid favours higher oxidation of the tin. As the latter metal must exist in the tin solution as protoxide, the tendency towards higher oxidation must be guarded against by dissolving the perfectly pure tin in concentrated hydrochloric acid, with exclusion of air and any higher temperature than a moderate degree of warmth. The simplest way to prepare the solution of protochloride of tin is by pouring concentrated hydrochloric acid over the tin, taking care that there is always a certain amount of tin in an undissolved state in the liquid. The clear solution is poured into a bottle containing a stick of metallic tin and tightly stoppered in order to preserve the contents from the oxidising influence of the air.

Another circumstance whereon the beauty of the colour in great measure depends is the degree of dilution of the gold and tin solutions; the more dilute the solutions the greater the beauty and purity of the resulting gold purple. The gold solution may be diluted until of a faint yellow tinge, but in the case of the tin solution care is necessary that the dilution be not carried to excess. The safest plan is to dilute the tin solution with eighty volumes of water, then set apart three or four portions in as many test glasses and attenuate these still further. Then by dipping a glass rod moistened with the gold solution into these test portions it can readily be seen which of the precipitates has the finest purple shade and the bulk can then be diluted accordingly. The flocculent precipitate of gold purple forms and gradually subsides; when all has settled down the supernatant liquid is poured off and the precipitate dried after several careful washings.

We now come to the precise description of the methods generally adopted for the preparation of gold purple, or, as it is also called, "purple of Cassius".¹ Most of the modifications of the process are concerned with the production of the aqua regia; each glass painter employs a particular ratio which he treats as a great secret and regards as producing the best solvent. The most renowned combinations are given below.

P. Robert employs the following proportion: Four parts 36° nitric acid and one part hydrochloric acid.

The purple is obtained by dissolving 0.63 gram of fine gold bullion in 30.59 grams of the above aqua regia. On the other hand 3.19 grams of chemically pure tin are dissolved in 22.94 grams of the same solvent diluted with an equal volume of water in order that the attack may be gradual. When solution is complete a further dilution with an equal bulk of water is performed, and the liquid, after filtration, added to the gold solution, which has also been greatly diluted.

Bunel prepares aqua regia from four parts nitric acid, one part hydrochloric acid, and ten parts distilled water.

The chloride of gold solution he makes by dissolving five grams of gold in the aqua regia, which must not be in excess; the protochloride of tin solution is prepared by dissolving fifteen grams of tin in aqua regia and immediate dilution with five grams of water.

Buisson uses an aqua regia composed of three parts 36° nitric acid and one part ordinary hydrochloric acid, in which he dissolves two parts of tin. The aqua regia for dissolving the gold is different, *viz.*: one part nitric acid and six parts hydrochloric acid, this being employed for the solution of seven grams of gold. No more solvent should be used than is absolutely necessary. He also prepares another solution

¹ From Cassius of Leyden, who first prepared it, in 1683.

of tin by one part rasped tin and three parts hydrochloric acid.

The gold solution is further diluted with three and a half litres of distilled water, the nitrohydrochloric solution of tin added and the purple precipitated by adding the tin chloride solution drop by drop until the precipitate has become of the colour of old red wine.

In order to more easily obtain the proper mixture of the two chloride compounds of the tin, P. Bolley makes use of "pink salt" (consisting of 70·80 per cent. of tin protochloride and 29·20 of ammonium chloride), which must be free from water and of constant composition. Ten grams of "pink salt" are mixed with 1·07 grams of metallic tin and the whole warmed, with an addition of forty grams of distilled water, until the tin is all dissolved, whereupon a further 140 grams of water are added. This liquid is employed to precipitate a gold chloride solution made by dissolving 1·34 grams of gold in aqua regia (without excess of acid) and diluting with 480 grams of pure water.

At the Sèvres Porcelain Works the following method of preparing gold purple is adopted. The aqua regia consists of 10·200 grams 36° nitric acid and 16·800 hydrochloric acid. One gram of fine gold is dissolved in eighteen grams of this acid, and when solution is effected the liquid is filtered and diluted by twenty-eight litres of water, which gives it the well-known straw-yellow colour. Thirty-six grams of the aqua regia are now taken and shaken up with ten grams of distilled water (in warm weather, or six grams if it is cold), and the vessel kept as cool as possible by immersion in a beaker of water. Six grams of fine Malacca tin filings are thrown into the vessel and are slowly and completely dissolved. The solution is passed through filter-paper and stirred into the gold solution; the precipitate subsides in the course of an hour or so and is carefully washed with

boiling water after the supernatant liquid has been decanted off.

Brongniart recommends this preparation with good reason, since, as he remarks, by means of this method, wherein everything is accurately weighed, an equally good result can always be obtained, provided the directions be complied with. This is confirmed by the author's own experience.

Several analyses of gold purple, showing that preparations made according to different prescriptions differ materially in composition, are appended. At any rate it is proved that the preparation may yield a fine red colour of various shades, such as scarlet, carmine,¹ rose, flesh colour, etc., or a violet or brown, according to the larger or smaller proportion of tin present and the lower or higher stage of oxidation existing in the solutions.

Gold Purple.	Gold.	Stannic Acid.	Water.	Analysed by.
Fine, without water - - -	24.00	76.00	0.00	Proust
Fine - - - - -	79.40	20.60	0.00	Oberkamp
Violet, without water - - -	40.00	60.00	0.00	"
Fine " " - - -	28.50	65.90	0.00	Buisson ²
Fine - - - - -	28.35	64.00	7.65	Berzelius
Fine - - - - -	19.00	not wgd	—	Fuchs
Dried and Brown - - -	21.00	"	0.00	Bolley

There still remain to be mentioned the methods of producing several preparations chiefly serving to form with gold purple a variety of shades of pale-red and dark-red colours used in glass painting.

Dr. Fuchs' Method of Producing a Beautiful Purple.

A solution of ferric chloride is dropped into and shaken up with a solution of protochloride of tin until the latter

¹ Chiefly produced in conjunction with silver chloride.

² Badly washed and contained 5.60 of chlorine (*Annales des Mines*, 1832, p. 400).

acquires a greenish tinge. It is then diluted with water and added gradually to the somewhat dilute solution of gold. The flocculent, pale-red precipitate is carefully washed and dried.

C. F. Capaun describes another mode of preparation by adding to a solution of ferric chloride three parts of water until the mixture assumes a greenish tinge. Six parts of water are then added and the flask containing the liquid set in a cool place until the gold solution is ready. The gold to be dissolved has the pure hydrochloric acid poured over it, and when this has been heated to boiling the nitric acid is gradually added until solution is complete. In this case also no excess of acid is permissible. The solution is now suitably diluted with distilled water and the iron-tin solution slowly added until no further precipitate forms, the addition being accompanied by continued stirring. The precipitate is brown and produces a beautiful purple colour.

IRIDIUM OXIDE.

The employment of this oxide in our branch of painting is limited to black, in which colour it yields finer and more stable pigments than can be obtained by the usual mixtures of ferric—and cobalt oxide, or ferric—and manganese oxide.

Iridium occurs in platinum sand, partly in the actual platinum granules, partly in separate granules associated with osmium; the black residue left after dissolving platinum sand in aqua regia, consists of iridium and osmium together with mechanical admixtures of chrome iron and titanitic acid.

Iridium is readily obtained from the black residue from platinum ore, by fusing the latter with potassium nitrate in a porcelain retort and washing out the mass with water. It is then distilled with nitric acid on the water bath, a good deal of osmium passing over. (The latter forms very noxious

vapours, so precautions should be taken against them.) Hydrochloric acid is added slowly and distillation proceeds until the odour of osmium ceases to appear in the test samples. Then follows the gradual evaporation of most of the acids, and extracting with water, the residue being treated anew with potassium nitrate and finally evaporated, whereupon potassio-iridium chloride conglomerates in black octahedra. This residual salt, being heated in a current of hydrogen, resolves into iridium and potassium chloride.

According to Frémy a similar method is pursued by heating to redness for an hour a mixture of one part of platinum residue and three parts of potassium nitrate. The resulting mass, consisting of the osmate and iridate of potassium, is treated with nitric acid to displace the osmic acid, and after dissolving out the potassium nitrate formed, the rest is treated with hydrochloric acid with a view to solution. Ammonium chloride being now added, a brown precipitate of osmium chloride and iridium chloride is obtained; to completely separate these two double salts a current of sulphurous acid gas is passed through the liquid, with the result that the iridium, parting with chlorine, is liberated and becomes readily soluble in water, leaving the osmium behind as an insoluble double salt. The liquid retaining the iridium in solution is filtered off from the osmium precipitate, and when heated along with two parts of potassium carbonate, yields perfectly pure iridium sesquioxide.

Pure iridium is white, very hard and brittle, and is infusible at the strongest white heat of our furnaces. It remains unoxidised under the influence of heat and air, and is almost insoluble in any acid, even aqua regia exerting little action upon it. On the other hand, when fused along with pure potash in air, it is oxidised and becomes soluble in acids, the solutions being blue, green or red, according to the degree of oxidation attained, and those in sulphuric and nitric acids

violet. To this variegation of colours the metal owes its name. There are four oxides, obtained by decomposing the chlorine compounds with alkali (as above): Protoxide, a sesquioxide, a trioxide and a sesquioxide, the second of which is the most important for our purpose. This is also the most stable of the oxides, since it remains undecomposed at red heat. It is a black powder, reducible by hydrogen gas—even without heat—and when heated with other combustible bodies detonates loudly. According to Brongniart, it is composed of:

Iridium	.	.	.	.	.	89.16
Oxygen	.	.	.	.	.	10.84
						100.00

COPPER OXIDE (CUPRIC OXIDE).

Copper has a peculiar brownish-red colour, possesses a characteristic astringent metallic taste and evolves a characteristic odour when rubbed with the hand. It has a high lustre, and in elasticity and hardness comes next after iron and platinum. The fracture is close grained, sometimes uncular. When a piece of bright copper is heated in air the surface is tinged with various colours (yellow, blue, violet) as the result of the formation of a layer of oxide of varying thickness. Finally, when heated to redness, it becomes coated with a dark-brown scaly layer, the so-called "copper scale," or "copper ash," which consists of the protoxide. This oxide is more refractory than the metal itself, but by prolonged exposure to red heat in the air it turns blackish brown (by complete oxidation to cupric oxide), and finally may be fused in a smelting furnace to a red-brown glaze. The oxide may also be prepared by roasting cupric nitrate or carbonate,¹ and this is, in fact, the method adopted for our

¹ Cupric nitrate is denser than the carbonate, and is more suitable for the purpose.

purpose. The cupric nitrate is prepared by dissolving thinly rolled fine rosette copper in dilute nitric acid, taking the precaution to add the copper, cut into small pieces, gradually, in order that the effervescence may not be too violent and cause the acid to suddenly lose all its oxygen. As soon as one piece of copper is dissolved another is added, and so on until saturation is complete.

Then follows heating the copper solution to redness in an ordinary crucible filled about one quarter full. The liquid rises to the brim of the crucible when boiling, and it is necessary to repeatedly blow on the surface (with a bellows) to prevent boiling over and to make the mass subside. When the liquid is nearly all evaporated more is added, and the operation continued until the whole is dry, whereupon the crucible is heated to redness. At this stage care is necessary not to raise the temperature too suddenly, otherwise the copper oxide will assume a grey colour, and will adhere to the crucible so strongly as to be difficult of removal. When the fire is not too strong the resulting oxide is a very fine, handsome black powder.

Cupric oxide has been used for blue, green and black pigments from the most ancient times; the Chinese make use of copper by a process unknown to us, and obtain thereby very handsome red and purple colours.

COPPER PROTOXIDE (CUPROUS OXIDE).

When a solution of cuprous chloride is boiled for a short time with metallic copper, or when fifty-seven and a half parts of black cupric oxide and fifty parts of very finely divided metallic copper—prepared by precipitation on a plate of iron from hydrochloric solution—are ground in a mortar and transferred to a closed bottle containing hydrochloric acid, an orange yellow solution is formed, wherein the copper

exists in the condition of protoxide, the oxidation of the copper having been effected at the expense of a part of the oxygen in the cupric oxide. Cupric oxide may also be prepared in other ways; by digesting metallic copper with ammonia a solution is formed which, when kept stoppered, will remain colourless for a long time, but oxidises so rapidly in the air that if a thin stream of the liquid be allowed to fall through the air a distance of one metre (thirty-nine and one-third inches) it will have turned blue during its passage. So long as the ammonia remains unsaturated the blue coloration may be removed by inserting more copper, but it will return on exposure to air.

The easiest method of preparation is that of Malaguti.¹ One hundred parts of cupric sulphate are heated with seventy-five parts of crystallised sodium carbonate at a moderate heat until the whole has solidified. The mass is then pulverised and mixed accurately with twenty-five parts of copper filings and exposed to white heat in a crucible for twenty minutes. On cooling it is powdered and washed, the residue consisting of red cuprous oxide, the colour of which will be finer in proportion to the degree of comminution attained and the thoroughness of the washing.

Cuprous oxide is a red, easily fusible substance, which, when heated in air, is converted into the black oxide. The protoxide colours glass fluxes ruby red, but is easily oxidised to cupric oxide, which produces green. Copper may be detected in glass fluxes, even when not betrayed by its colour, by means of the blowpipe, the addition of a little tin to the bead producing a transparent red when little, and an opaque red when much, copper is present; extraneous metals often turn the colour almost black.

Cuprous oxide contains :—

¹ *Annales de Chimie et de Physique*, vol. liv., p. 217.

Copper	-	-	-	-	-	88·78
Oxygen	-	-	-	-	-	11·22
						100·00

COBALT OXIDE.

Cobalt is greyish white in colour, with a tendency towards a reddish tinge; it is hard and brittle, with a coarse-grained fracture, resembles iron, is very difficult to prepare, and is, in fact, only produced occasionally as a rarity for the laboratory or for scientific experiments. It is generally met with in combination with sulphur and arsenic, or associated as oxide with other metallic oxides, and these minerals are chiefly employed for preparing the protoxide and oxide, or their salts, which latter are used subsequently for the manufacture of pigments. The most common are cobalt glance (with sulphur and arsenic) and smaltine (with arsenic and iron); furthermore, nearly all meteoric stones contain cobalt.

Cobalt does not undergo any important alteration at ordinary temperatures, either in air or in contact with water; but on prolonged exposure to red heat, or when roasted, with access of air, it oxidises without fusing. The resulting oxide is dark blue (somewhat reddish when accompanied by arsenic), passing into a dark blue glass—cobalt protoxide—at a strong smelting heat. This consists of:—

Cobalt	-	-	-	-	-	83·5
Oxygen	-	-	-	-	-	16·5
						100·0

On prolonged heating to faint redness it takes up more oxygen, assumes a perfectly black colour and becomes cobalt oxide (black oxide), consisting of:—

Cobalt	-	-	-	-	-	80
Oxygen	-	-	-	-	-	20
						100

Heated to moderate redness it reverts to the condition of protoxide and regains its blue colour. Both oxides may also be prepared in the manner detailed below.

The protoxide of cobalt is contained in all the cobalt salts, and is dissolved by acids without any evolution of gas. On the other hand cobalt oxide is only soluble in acids after a preliminary deoxidation (to protoxide), and when dissolved in hydrochloric acid chloride vapours are given off; in the case of sulphuric acid and nitric acid the evolved gas consists of oxygen.

Nitric acid forms the most suitable solvent for cobalt; the metal, as well as the protoxide and oxide—the latter by the aid of heat—dissolving readily with evolution of nitric acid fumes. The solution is rose-red in colour, and on concentration and evaporation yields small prismatic crystals of cobaltous nitrate, which liquefy on exposure to the air and are soluble in alcohol. On heating the crystals in a retort until nitric acid fumes are given off, black cobalt oxide is left behind.

Sulphuric acid will only dissolve cobalt when concentrated and heated, whereby sulphurous vapours are evolved, but the oxides, and particularly the protoxide, dissolve more easily. The red crystals obtained from the reddish-coloured solution dissolve in twenty-four parts of water, effloresce in the air (turning blue when deprived of their water of crystallisation by heat), and, according to Buchholz, consist of:—

Sulphuric acid	-	-	-	-	-	26
Cobalt oxide	-	-	-	-	-	30
Water	-	-	-	-	-	44
						100

On prolonged heating to redness they leave cobalt protoxide; this salt is occasionally also met with in minerals.

Hydrochloric acid, too, dissolves cobalt only when con-

centrated and aided by heat, but the oxides are more soluble. The saturated solution is red, but when free acid is present—in a concentrated condition—the colour is green, as also when warmed; on dilution with water the solution again becomes red. When evaporated and cooled a garnet-red salt—cobaltous chloride—is left behind; this is deliquescent and is also soluble in alcohol. In the fire a portion of the salt sublimes, leaving the remainder behind as cobalt oxide.

After this short exposition of the chief properties of cobalt and its oxides, we now proceed to the consideration of the various cobalt compounds as regards their employment in painting, and will then pass to the various methods employed for the preparation of cobalt carbonate.

Glass fluxes coloured with cobalt oxide are blue in daylight but by candle-light are violet, or, when the amount of oxide is very small, reddish; a very small quantity of oxide is sufficient to colour the glass strongly, and if too much is used the glass becomes black. Borax fused with cobalt oxide and then dissolved out by water in a closed vessel leaves it behind as a bulky blue mass. When heated with borax on a porcelain plate the oxide is more highly oxidised and yields a black mass which forms with manganese a fine, black enamel pigment.

The preparation of cobalt from its ores is very difficult. The ores are first freed from gangue, and in case they contain bismuth must be refined to get rid of the latter. They are then stamped in the dry state and roasted in a calcining furnace, where they are stirred continually with iron poles. In this process arsenic escapes as white oxide and is collected in the arsenic chimney in connection with the furnace. On removal from the furnace the ore is sifted and the large lumps returned to the stamping-mill. This oxide is, by reason of the arsenic and iron present, either reddish or bluish-green in colour, and is known as zaffre. It is now

mixed with fine sand or crushed quartz (two or three parts), moistened a little, and packed in barrels for sale under the above-mentioned name. It is used as a blue glaze for low-grade pottery, as well as for the production of ordinary blue glazes.

Smalt is a similar product used for the same purposes, and is prepared by dry mixing the roasted cobalt ore with larger or smaller quantities—according as the product is to be paler or deeper in colour—of crushed quartz, or quartz sand, and potash, in the ratio of eight to nine parts sand, and five to six parts potash, to two (and more) parts cobalt ore, and is then fused in a glass furnace in the manner usual in making glass.

As the blue colour yielded by cobalt oxide is finer in proportion as the oxide is purer—especially as regards freedom from iron—the merely roasted cobalt ore cannot be employed for producing a fine blue colour in glass, porcelain and enamel, but a more highly purified oxide is necessary for that purpose.

The presence of nickel in quantity also produces a dirty blue colour, and as the cobalt preparations are among the most susceptible, *i.e.*, will only produce pure shades of colour when themselves perfectly free from compounds of iron or nickel, it becomes advisable to prepare them oneself. Paul Randau, in his work on enamel (*Die Fabrikation der Emaille*), remarks on this point as follows, and his observations apply not only to enamels but also to the preparation of glass colours and porcelain glaze colours as well.

Cobalt is now employed almost exclusively for the production of blue colours for enamel, there being no other material yielding so well or producing such fine colours. It may be employed in various forms, as protoxide, chloride and so on, as well as in the condition of silicate, the so-called smalt. The commercial smalts are, in the higher

grades at least, very good in colour, but still not good enough for use in the finer kinds of enamel. It is therefore important, both for this object and for enamel painting, to have cobalt preparations free from foreign materials, especially such as may act prejudicially on the colour. The very best preparation for this purpose is cobaltous silicate, and no manufacturer producing coloured enamels should neglect to make this preparation for himself, since in beauty of colour it far surpasses the products generally employed. We therefore append a description of the rational method of making this preparation.

Cobaltous Silicate.

For the production of this substance the cobalt ores, cobalt glance, smaltine, etc., can be used. The ore is reduced to a coarse-grained powder and roasted with unrestricted access of air, whereby the greater part of the arsenic, present in many cobalt ores, is volatilised in the form of arsenious acid (white arsenic).

The residue is stirred up to a thick gruel with concentrated sulphuric acid, and is then heated to strong redness in a furnace and treated with water. The cobaltous sulphate produced by the sulphuric acid treatment possesses the property of withstanding very high temperatures without decomposition, whilst most of the other oxides in the ore form salts, which are thereby transformed for the most part into oxides or very insoluble basic salts.

When the roasted mass is brought into contact with water only a small amount of ferrous sulphate passes into solution along with the cobaltous sulphate. To remove the former, small quantities of soda solution are added to the liquid. This causes, in the first place, the deposition of iron oxide from the solution as a brown precipitate, and with a

little practice the moment when the last trace of iron oxide has come down can be sharply defined. Immediately cobaltous carbonate begins to precipitate, it is recognisable by its pale blue colour.

The cobalt solution, now free from iron, is next filtered from the ferric hydrate precipitate, and cobaltous silicate is thrown down, as a pale blue sediment, by means of a solution of waterglass (sodium silicate). This precipitate is washed, dried and fused, and then forms a very dark but pure blue mass, which is particularly suitable as a pigment for enamel. A certain quantity of this compound—after being poured in a fused state into water and powdered—suffices, when mixed with the “mass” of enamel, to produce a beautiful blue flux.

It would appear that the quality of the enamel “mass” which this preparation is employed to colour, exerts great influence on the intensity of the tone, and it is, therefore, necessary to ascertain, from time to time, by fusion tests, the precise amount of cobaltous silicate requisite for the production of any given shade.

COBALTOUS ZINC PHOSPHATE.

This preparation is employed for the production of very fine and pure toned cobalt colours and pigments. The simplest method of preparing this double salt is by adding to a solution of sodium phosphate first a solution of zinc sulphate and then a solution of cobaltous sulphate, the addition of the latter being continued until the initially green precipitate assumes a deep blue colour.

This particularly fine blue is usually applied as a flux, consisting of two parts of sand and lead oxide and forty-two parts of the double phosphate, to which has been added eight parts of pure cobaltous oxide.

By suitably increasing or diminishing the proportion of the colouring cobalt compounds, all varieties of tone from pale to the very deepest blue can be produced.

Whatever be the cobalt compound used for colouring the enamel mass care must be taken to see that the cobalt oxide is as far as possible free from certain oxides, which exert a damaging influence on the purity of the colour. Among these the protoxides of nickel and iron and the oxide of manganese are the most injurious; the other metallic oxides, although destructive of the purity of tone, not being so to the same extent as the three first named.

An admixture of nickel, which is practically never absent from cobalt ores, causes the colour of the enamel to appear violet so long as it is in the heated condition, altering to brown in cooling, and finally giving a reddish tinge to the blue when cold.

A very small amount of ferrous oxide suffices to give the blue a greenish cast; ferric oxide produces a similar but less decided effect than an equal amount of ferrous oxide, and it is therefore advisable, when the preparation cannot be obtained free from iron, to convert the latter into the ferric condition by means of oxidising agents. To this end arsenious acid, saltpetre, or, in fine, any substance capable of yielding up its oxygen at a red heat, is added to the enamel.

The effect of manganese oxide is to impart a violet shade to the blue, whereas the protoxide of this metal has no evil influence on the colour. If the protoxides of manganese and iron are present together, their action on the colour is neutralised.

Smalt.

Of all the preparations of cobalt used for colouring glass or enamel masses none is so frequently employed as that

obtained from the "blue" works of Saxony under the name of smalt.

As far as chemical composition is concerned, smalt is a glass, coloured an intense blue by means of cobalt, and with reference to its composition and colouring properties, approximating nearest to cobalt silicate.

A description of the manufacture of smalt does not fall within the province of this section of the present work, because no enamel maker will prepare this himself but will obtain it from the manufacturer. We will, therefore, merely indicate the general outline of the process.

Cobalt ore is roasted in such a manner that the cobalt is mainly in the condition of protoxide; the other metals not being oxidised, but chiefly separable as arsenides in the subsequent smelting process, and constituting an important source of nickel.

The roasted ore is then fused with potash and silica, producing a cobaltous oxide potash glass. By pouring this glass into cold water it is obtained as a brittle mass, which is then stamped to fine powder and subjected to a very tedious process of sedimentation.

This last treatment results in the separation of the powder in very different degrees of fineness, the intensity of the colour depending to some extent on the degree of division attained. A fundamental condition of the employment of smalt in enamel making, especially when fine enamels are in question, is that only the finest grades of smalt should be used; these will give a blameless product in all cases where it is not a question of the attainment of the very highest degrees of beauty of colour.

Protoxide of cobalt yields better, in respect of colour, than almost any other oxide, on which account only a very small quantity of smalt is required to produce a very dark shade of blue. The relative cheapness ensuing therefrom is the

reason for the employment of cobalt protoxide for very ordinary grades of enamel, such as, for example, is now used for enamelling the outside of cooking utensils.

ZAFFRE.

This product, also erroneously called "safflower," consists of finely powdered, roasted cobalt ore, and since it, of course, contains all the foreign oxides present with the protoxide of cobalt, is consequently incapable of producing fine colours. The proportion of protoxide of cobalt contained therein being, moreover, very variable, it is always necessary to make trial fusings before any idea can be gained of the action of this product.

It must also be mentioned with regard to preparations of cobalt that they are not seldom employed for imparting a pure white colour to enamels rendered slightly yellow by the presence of small amounts of ferric oxide, the blue produced by cobalt protoxide being complementary to the ferric oxide yellow, and the mixture therefore forming white.

If, then, it is desired to make such a yellow enamel pure white, a small quantity—determined by a few fusion tests—of some preparation of cobalt is added, and this manipulation results in the production of an enamel perfectly pure white to the eye. Should, however, any excess of cobalt be employed, the colour of the latter will preponderate and the enamel will acquire a bluish, *i.e.*, milk white, tinge.

By admixture with yellow or green colouring pigments all the conceivable stages between blue and these colours can be produced by the aid of cobalt preparations. On account of its ability to withstand fire and the purity of its colour, cobalt protoxide constitutes one of the most valuable pigments at the disposal of the enamel manufacturer.

In preparing cobalt colours in small quantities for experi-

mental purposes it is advisable to use the cobaltic nitrate, now obtainable in commerce in a very pure state. This yields pure cobalt oxide when heated to redness. The aqueous solution of cobaltous nitrate produces with soda solution a pale red precipitate of cobaltous carbonate, which, when washed and dried, may also be fused to a coloured glass along with silica, borax, etc.

MANGANESE OXIDE.

The crude oxide of manganese from which the pure oxide is prepared is very frequently employed in painting glass, porcelain, enamel and earthenware, and a whole range of browns and blacks can be obtained by its aid.

Manganese has a silvery colour, inclined towards grey; it is hard, brittle and very refractory, fusing only at 160° Wedgwood. It readily oxidises in the air, and finally falls down into a black powder; in contact with water it oxidises at ordinary temperatures, hydrogen being liberated.

The natural oxide of this metal has been known for a long while, but the metal was first prepared from it only in 1770.

The black or brown manganese oxide, when fused with borax or glass, forms a red-coloured glass, varying from violet to black (or more properly, a deep dark violet) in shade, according to the amount of oxide taken. The state in which the manganese occurs in this combination is that of red or brown oxide. When in a lower state of oxidation the glass is not coloured. When borax glass is fused with a small quantity of black oxide of manganese on charcoal before the blowpipe, the resulting bead is clear and colourless, but if the bead be warmed in an illuminating flame it assumes a violet coloration, persistent on cooling, because the oxide previously reduced by the charcoal or by the great heat employed, is now reoxidised by the air. On heating over again on char-

coal the colour will again disappear. The same occurrence takes place when manganese oxide is fused with silica glass, the glass coloured red by this oxide losing its colour when fused at a very high temperature or on charcoal; however, when softened at a lower temperature, with access of air, it regains its colour, and the same result ensues on the addition of potassium nitrate.

Used in small quantities manganese oxide is employed to decolorise glass. Mixed with a glass flux it imparts a violet colour to enamel and porcelain. In larger quantities, alone or along with copper and cobalt oxides, it serves to produce black, and for ordinary pottery the crude oxide is used in the preparation of black and dark-brown glazes.

Pure manganese oxide is prepared for our purposes as follows: Pure black (not violet-black) crude oxide is finely ground and treated with hydrochloric acid in the warm, water being added in suitable amount as soon as the evolution of chlorine ceases. Dilute ammonia being added to this solution a dark-brown precipitate is formed, which, after careful washing—six or seven times repeated—is dried and heated to redness. Heat is applied gently at first, then progressively stronger until red heat is attained, the mass being stirred all the time. After the calcination is finished the oxide is finely ground.

The simplest method of preparation is from the very cheap and pure commercial salt, manganese sulphate, by dissolving the rose-red crystals of this salt in water, adding ammonia so long as a precipitate continues to form, and filtering, washing and drying the latter; finally the oxide is completely freed from water by exposure to a red heat.

This latter method of preparation is preferable to that wherein the solution of manganese chloride, obtained by attacking the crude oxide with hydrochloric acid, is employed, because the crude oxide always contains variable

amounts of iron compounds, so that the precipitation of the solution by ammonia is not pure manganese oxide but is more or less contaminated by ferric oxide.

URANIUM OXIDE.

Uranium, which was first prepared in 1789, by Klaproth, from the so-called pitch blende and was named after the planet Uranus, then recently discovered by Herschel, is a hard, brittle, very refractory iron-grey metal. When heated in air the metal at the commencement of red heat glows like coal, swells up and finally falls apart as a soft powder (greyish-black when cooled), uranium protoxide, which contains about five per cent. of oxygen. This oxide may also be prepared by decomposing the sulphate or chloride of uranium at a red heat. Nitric acid forms the most suitable solvent for uranium and its oxides; the yellow solution yields tabular citron-yellow crystals of uranium nitrate which are readily soluble both in water and alcohol and deliquesce on exposure to the air. When decomposed by heat they leave behind the oxide as a yellow-brown powder, inclining to green. A yellow uranium oxide is precipitated by potash from the nitrate solution.

Uranium oxide is dissolved more or less readily, to a yellow-coloured solution, by all acids. By itself it is infusible at high temperatures, and does not undergo deoxidation thereat.

When fused with potash-glass fluxes it imparts to the latter a more or less brown-yellow coloration, varying with the amount employed, and produces in conjunction with the necessary glass fluxes a full, orange-yellow colour on enamel or porcelain.

The crystalline uranite contains this yellow oxide only, and citron-yellow in colour, or merely tinged with green

from traces of cupric oxide. Pitch blende, or black uranium ore, from which the yellow oxide is prepared, contains, in addition to uranium protoxide, a little lead sulphide, ferric oxide, and frequently copper oxide and silica.

For our purpose uranium oxide may be prepared by finely pulverising the pitch blende; digesting it with nitric acid until reaction ceases; then filtering the solution, drying by evaporation, re-dissolving in water and throwing down the oxide by the addition of dilute ammonia until precipitation ceases.

The resulting uranium oxide still contains a little ferric oxide. In order to free it from the latter, proceed as before by precipitation with ammonia; continue to add this reagent until the uranium oxide is re-dissolved and then heat to boiling, whereupon the pure uranium oxide will be re-precipitated. The oxide may also be precipitated by potash or soda, with which it combines, and we then have a darker yellow and more readily fusible precipitate. The colour is, however, not so good for our purposes, and it should be recollected that when these reagents are employed in the presence of earths or other metals the latter are also precipitated, a result which does not occur when ammonia is used.

According to Brongniart pure uranium oxide consists of:—

Uranium	-	-	-	-	-	94.75
Oxygen	-	-	-	-	-	5.25
						100.00

ZINC OXIDE.

Zinc is found native, partly in combination with sulphur, as blende, partly oxidised with silica or carbonic acid, as calamine, and partly as a sulphate, the so-called white vitriol. Zinc being volatile, the roasted calamine (or blende) employed

for its production is mixed with powdered carbon and placed in large conical crucibles provided with clay lids and fitted at the bottom with an iron pipe (passing through the hearth of the furnace into a receiver filled with water) through which the zinc is distilled. The heat must not be great enough to fuse the calamine, otherwise it would flow into the pipe. The zinc is melted over again and cast in moulds.

Zinc is a lustrous, bluish-white metal, which, when cooled, slowly crystallises in square or hexagonal prisms; it is almost inflexible and breaks with a crystalline fracture. When perfectly pure it may be beaten out into thin leaves at ordinary temperatures. Commercial zinc¹ is not so soft at these temperatures, but at 100° to 150° C. may be hammered or drawn out to very fine wire; at 205° zinc is again brittle and can be pounded to powder, and at 360° it fuses. At a white heat it boils and may be distilled in closed vessels, but burns in the air with a brilliant white flame and thick white smoke. At higher temperatures zinc has a strong affinity for oxygen and reduces most other metals; dry air and oxygen have no action on zinc, but when moistened the metal becomes coated with protoxide. In the absence of air zinc does not decompose water, but at red heat the vapour of water is split up by the metal. Nearly all acids dissolve zinc, with evolution of hydrogen, and many metals: copper, silver, mercury, etc., are precipitated from their solutions by this metal.

There are three oxides of zinc, the protoxide, the oxide and the peroxide, but as we are only concerned with the oxide, the other two will be left out of consideration. The oxide is precipitable by alkalis from solutions of zinc, or prepared by inserting small pieces of the metal in a fairly large crucible, inclined at an angle and heated to white heat, whereupon

¹ East Indian zinc is the purest commercial form and is especially suitable for our purpose.

they take fire, oxidise and partly escape as vapour, the rest remaining behind as a yellow-white wool, which is removed from the surface of the metal from time to time, so as to give access to the air. As soon as a certain amount of the oxide is collected it is removed by means of an iron scoop before the insertion of a fresh quantity of zinc. The freshly prepared oxide is luminous for half an hour in the dark, emitting a blue phosphorescence. In colour it is yellow when hot, white when cold, and it may be freed by sedimentation from any metallic zinc present. The oxide thrown down by alkalis from commercial zinc sulphate usually contains so much iron that it becomes dark green when heated to redness.

Pure zinc oxide, suitable for our purpose, is prepared by dissolving commercial zinc in sulphuric acid, precipitating the accompanying cadmium, lead and copper by sulphuretted hydrogen, boiling, filtering, adding "chloride of lime" solution in small doses so long as any precipitate—manganese and iron oxide—comes down; crystallising, whereby cobalt and nickel are separated in the mother liquor, then dissolving the crystals in a minimum of cold water; filtering from gypsum; diluting with water, and finally precipitating hot by an excess of sodium carbonate and heating the precipitate to redness.

A simpler, but at the same time much dearer, method of preparation is by the use of nitric acid, in which the zinc is dissolved along with any manganese and iron present, copper and lead being, however, unattacked. The solution is suitably diluted with water, and to it is added drop by drop an equally diluted solution of sodium carbonate. The precipitate first formed consists of ferric oxide, and must be removed at once. When the formation of ferric oxide ceases the addition of soda is continued to throw down the zinc oxide, which is then thoroughly washed and dried by moderate warmth.

Zinc oxide is of itself colourless and imparts no colour to

porcelain; it is none the less a very important substance on account of its great influence on the shading of the majority of pigmentary bodies.

Now-a-days zinc oxide is prepared on a large scale, and is used under the name of zinc white for making up into white paint. Since the finer qualities of commercial zinc white are almost entirely composed of zinc oxide, it is simpler for our purpose to employ the commercial article instead of making it ourselves.

TIN OXIDE (STANNIC OXIDE).

Metallic tin has a white colour of great lustre, a little more inclined to bluish than that of silver; it is very soft and but slightly elastic, fairly ductile and very malleable, so that it may be rolled or hammered out into thin sheets. It evolves a characteristic smell when heated or ground, and gives out a peculiar rustling sound when bent; it is readily fusible, and smelts at 182° R. (227.5° C.), much below red heat. Although, when exposed to the air at ordinary temperatures, tin gradually loses its superficial lustre and turns a whitish grey, it does not thereby suffer actual oxidation; if, however, it be fused, with access of air, the surface soon becomes covered with a grey skin, which, if moved aside, gives place to another, and so on until finally the whole of the fluid mass of tin has become converted into this grey powder. This forms the so-called tin dross, and consists of finely divided metallic tin and the protoxide, and may be easily reduced to the metallic state once more by fusing with charcoal. When tin dross is heated to redness in open vessels for several hours and frequently stirred, it oxidises further and is converted into a whitish-grey substance, tin protoxide or tin ash. If the metal be heated to redness in air it finally takes fire and burns with a small, bright, white flame, throwing out a white vapour—tin oxide—which settles down as a lustrous white powder.

Both oxide and protoxide of tin are very refractory, and, therefore, do not produce a transparent, but only a dull, white glass, with vitrifiable substances, since the tin compound remains in an infusible state diffused throughout the mass, to which it therefore communicates its whiteness.

Tin is very rarely obtainable pure, being generally mixed with lead; other metals such as copper, bismuth, zinc, antimony, arsenic and iron may be also present, though less frequently and in smaller amount. Even the best Cornish block and bar tin contains some two to four per cent. of lead. For our purpose Banka or Malacca tin is the best.

The preparation of tin oxide for glass, etc., painting is effected by treating finely divided Banka tin with nitric acid, and washing, decanting and drying the sediment produced. The most suitable way is to melt pure commercial tin and pour it as a thin stream into water, transferring the granules thus formed into a glass vessel, where they are suffused by a little fuming nitric acid. The reaction begins at once; suffocating brown red fumes are evolved (so that the work must be done in the open), and a white powder, consisting of tin oxide, forms on the surface of the metal. When the emission of vapour subsides more acid is added and shaken up, and this process is repeated until nearly all the tin has disappeared. Finally, a large quantity of water is added, and the tin oxide is separated by sedimentation from the unaltered tin, which is kept for use in the next operation. The heavy white powder of tin oxide is repeatedly washed and dried. It is quite white and soft, and consists of pure tin oxide with water of combination:—

Oxygen	-	-	-	-	-	19·05
Tin	-	-	-	-	-	70·24
Water	-	-	-	-	-	10·71
						100·00

which is driven off at red heat.

The oxide may also be prepared by precipitating tin chloride with an alkali, or, better, ammonia, no more of the reagent being added than is necessary to bring down the tin. The gelatinous precipitate is washed with water and dried, whereupon it turns to a vitreous mass, very hard to disintegrate.

In Brongniart's method the tin oxide is mixed with an equal weight of crystallised and perfectly white common salt, and the finely pulverised mixture placed in a platinum crucible (or porcelain in default of platinum) and calcined for three hours, whereupon the crucible is taken out and cooled. The resulting mass is carefully powdered, ground down fine with water on a glass plate, washed and dried at a moderate warmth.

Since lead oxide is, for our purpose, not only innocuous but sometimes desirable, the testing of the tin need not be very minutely performed.

A white tin oxide is met with in commerce (frequently under the name of "white enamel" or "calcine"), which consists merely of a mixture of tin oxide and lead oxide.

II. EARTHY COLOURS.

YELLOW OCHRE.

Two varieties of yellow ochre are generally known, the clayey (argillaceous) and the calcareous, the latter being less employed for our purpose. From the chemical point of view these colouring matters are a variety of clay mixed with ferric hydrate (the colouring principle).

Various yellow pigments are met with in commerce, some of them natural, some manufactured. We will only mention natural yellow ochre, which, occasionally tinged with red, is coarse or fine, soft and staining, and evolves a clayey odour when breathed upon.

The ochre colours are obtained by digging or mining, but since, in addition to ochre, they contain not unimportant quantities of sand they must be washed by sedimentation to separate them from the latter substance.

In ascertaining the colouring value of two or more samples of ochre the best information is afforded by the white lead test. This is performed by mixing equal parts (say ten grams each) of ochre and white lead and then grinding them in oil; the sample exhibiting the darkest shade will contain the most colouring matter.

It is most important for our purpose that the ochre should be used only in the finest state of division attainable by sedimentation, and, when dried, heated to redness with the quantity of flux determined on, or merely ground therewith, according to the shade of colour desired. Latterly the use of ochre and the following colours has decreased, partly on account of their variable constitution and partly because more accurate results are obtainable with other metallic pigments.

For the production of a fine yellow-brown colour with ochre four parts of finest elutriated and ground ochre, one part red oxide of iron (ferric oxide), and one part antimony oxide are intimately mixed with water and the whole poured into a high glass flask. At the end of four minutes the upper layer of turbid water is poured off into a clean glass and covered up. Fresh water is poured on to the sediment, which is well stirred up, and the turbid upper layer transferred, after three minutes, to the first pouring. This operation being repeated a third time, the thick sediment is removed and the pourings left to stand for eight days, to be then decanted for the last time, the soft pigment then left being dried in the air and stored for use.

RED OCHRE.

When yellow ochre is immersed in water it falls to pieces therein, and if this ochre be exposed to red heat it yields red ochre, which is merely the yellow earth calcined. A few analyses of ochre are appended, showing its quantitative composition :—

Ochre.	Water.	Alumina.	Ferric Oxide.	Lime.	Analysed by.
Yellow, No. 1 - -	21.43	—	78.57	—	Proust
" " 2 - -	7.00	69.50	23.50	—	Berthier
" " 3 - -	(?) 9.00	74.40	26.60	—	"
" " 4 - -	7.60	80.00	12.40	—	"
Red, " 1 - -	—	74.00	20.00	5.00	Merat-Guillot
" " 2 - -	—	94.00	3.00	3.00	"

TERRA DI SIENNA.

Under this designation an earthy body (also known as Italian earth) of yellow-brown appearance, with a conchoidal fracture exhibiting a brown, pitchy lustre and consisting of hydrated ferric oxide with variable proportions of manganese hydrate, aluminium and sulphuric acid, occurs. This colouring matter is prepared by finely grinding the commercial Terra di Sienna, which is then subjected to a process of washing by sedimentation, as in the case of ochre, and, when dry, heated to redness in a crucible. The calcined mass is thrown into water, left for a few days, and then heated once more to redness, care being taken to allow the crucible to cool down gradually. The resulting pigment (which in an impure state is met with in commerce as "mahogany brown") is ground down very fine in water and stored for use. About thirty-five per cent. of the Terra di Sienna is lost by the calcination, this amount chiefly consisting of the sulphuric acid and water thereby driven off.

The best way of testing the various grades of "raw" and

“burnt Sienna” is by rubbing the samples down very fine, spreading them side by side on a glass plate and holding them against the light, which enables the variations of brilliancy, lustre and tint to be most suitably determined.

UMBER.

The various colours known under this name, and also as umber brown, are earthy pigments which consist mainly of calcareous ochre, but range in shade from pale to deep brown, and almost to black. The constituents of these colours are, as in the case of ochre, chiefly ferric oxide, ferric hydrate and ferro-ferric oxide, along with varying proportions of manganese oxide, lime, sand, etc., on which account they are rendered darker, but in all cases redder, by burning, owing to the conversion of the ferric hydrate into oxide.

The umbers are burned by the “umber washers” (Thuringia), and put on the market as burnt umber. For the purposes of the glass and porcelain painting industry the burning is performed in the manner described in the case of Sienna.

A few analyses performed by Brongniart are appended, and show the varying quantitative composition of the Siennas and umbers :—

	Water.	Silica.	Alumina.	Lime.	Magnesia	Ferric and Manganese Oxide.
Umbur, No. 1 -	17·10	15·00	12·11	0·27	Traces	55·27
„ „ 2 -	16·07	21·00	13·00	0·46	Traces	48·76
„ „ 3 -	20·00	23·00	6·47	1·18	0·70	48·00
„ „ 4 -	15·17	23·62	16·00	3·75	1·00	40·00
Terra di Sienna, 1	9·50	11·45	5·85	Traces	Traces	73·20
„ „ 2	8·76	9·00	2·00	0·16	0·07	80·01
„ „ 3	17·90	5·00	Traces.	Traces	1·10	76·00

MARS YELLOW.

Instead of the natural ochres, a preparation obtained by artificial means and very suitable for our purpose may be

used. This is the so-called "Mars yellow," generally consisting of a mixture of ferric oxide and gypsum or alumina. It is prepared by mixing a solution of ferrous sulphate with milk of lime, which causes the precipitation of ferrous oxide as a pale-brown deposit; on exposure to air the colour becomes yellow-brown owing to the rapid oxidation of the protoxide. On heating the precipitate, Mars yellow is obtained in various shades, ranging between yellow and red, according to the temperature employed. In addition to Mars yellow, Mars orange and Mars red are also met with in commerce.

The preparation of this pigment is a very simple matter. One part, by weight, of ferrous sulphate is dissolved in ten parts of water and added to a milk of lime made from one part, by weight, of lime and forty parts of water. When it is a question of preparing a product which shall have a dark colour—and especially for Mars orange—the amount of ferrous sulphate should be increased to two parts.

After uniting the solutions the mixture must be stirred up for some time to effect intimate incorporation. The mixture, which is at first an ugly grey colour, rapidly assumes a ferric hydrate coloration in the air, which ordinarily deepens on drying.

If the dried and ground Mars yellow be heated to redness in thin layers the colour changes to dark yellow, and finally to orange red. The alteration is similar to that occurring when ferric oxide is heated to redness by itself.

A variety of Mars yellow can be produced from a mixture of ferric oxide and alumina instead of lime and ferric oxide. This colour, which is still more brilliant than that prepared from lime, is produced by simply mixing the ferrous sulphate solution with a solution of alum and throwing down the mixture with caustic soda. This precipitate consists of alumina and ferric oxide. In order to prevent an undesirable efflorescence of sodium sulphate on the surface of the dried

product, care must be taken to completely remove this salt by washing.

When strongly and continuously heated to redness, Mars yellow changes finally into a very fine brown pigment, employed under the name of Mars brown.

III. METALS.

Under this heading we shall treat of two metals, gold and platinum, which, however, are not employed as true pigments, but used, on account of their characteristic lustre, for decorative purposes. Silver and copper were also used in the same sense formerly, but, being insufficiently durable, are no longer employed. Gold and platinum possess in the highest degree the properties required of such metals as are to be applied with a brush when in a state of extremely fine powder, namely, great ductility and power of resisting light, fire, and other weak (chemical) influences. Silver and copper are also endowed with these properties to a certain extent, but readily become oxidised by the sulphur compounds frequently generated in dwelling-houses and thereby lose both lustre and colour.

GOLD.

For the gilding of porcelain gold is generally employed in three forms, *viz.* : as gold powder prepared with ferrous sulphate ; gold powder precipitated by mercurous nitrate ; and mussel (shell) gold.

Precipitation by Ferrous Sulphate.

A solution of gold in aqua regia is prepared and the clear solution divided into four equal parts, each of which is diluted with distilled water. To each of these liquids a filtered solution of ferrous sulphate is added so long as

a precipitate continues to form, and after leaving the precipitate to subside during a few hours the supernatant liquid is poured off and the residue, after a careful washing with water, is dried on the water bath. It may happen sometimes that a small amount of ferric oxide is also thrown down, but this can be re-dissolved in a little hydrochloric acid. The action of this acid is, however, always injurious, causing the molecules of gold to agglomerate and harden, whereby their distribution by the brush is rendered more difficult.

Precipitation by Mercury.

According to Salvétat the gold to be precipitated by mercury is most easily prepared by dissolving 250 grams of distilled mercury in 500 grams of nitric acid in the warm. Simultaneously a solution of 30 grams gold in 350 grams nitric acid and 75 grams hydrochloric acid is prepared, and the two solutions are then mixed by adding the mercury solution in small doses to the gold solution. A voluminous mass, which consists of nothing else than very finely divided gold, is obtained, and this is very carefully washed, dried in a water bath and bruised on a silk sieve. The gold produced in this manner is more finely divided than that precipitated by ferrous sulphate, although this—apart from the larger quantity of gold required and the consequent increased cost of the gilding—presents the advantage of producing a more solid and durable coating.

Mussel Gold.

Mussel gold—which owes its name to the circumstance that this (mechanically prepared) gold is generally precipitated in mussel shells—forms the most expensive gilding material, owing to the expense of, and long time occupied by, the method of preparation. According to Brongniart, fine

gold leaf is taken and rubbed down on a glass plate along with pure honey, sugar,¹ sea salt, or any other substance readily and completely soluble in water. When the gold has been brought to a sufficiently fine state of division, the mass is shaken up in a vessel filled with warm water, which is stirred to facilitate the absorption of all the soluble matter, and the gold powder is left to subside, decanted and dried on the water bath. A skilled workman can only prepare about 60 grams at most per diem.

The task of grinding the gold is a very tedious operation, and considerably increases the cost of this already expensive material. This task can, however, be reduced considerably by first bringing the gold to a finely divided condition by chemical means.

The gold can be obtained in an extreme state of comminution by pouring hydrochloric acid over gold in any form—coins, broken ornaments, etc., are all equally suitable—and gradually adding nitric acid to the heated liquid. The gold dissolves readily in the acid mixture, and there only remains—in case the gold has been alloyed with silver—a white deposit of silver chloride, which can be separated by filtration from the (greatly diluted) solution of gold. The latter is boiled for a while to drive off the excess of nitric acid and then treated with an aqueous solution of ferrous sulphide, whereupon it immediately turns a bluish-black colour, and soon after deposits a brown sediment of chemically pure gold, which is in such an extremely fine state of division that its lustre has almost completely vanished.

This precipitate is filtered off from the liquid and may be stored in closed bottles when dried. To prepare mussel gold from this powder it is only necessary to incorporate the requisite quantity of gold with a thick solution of gum by grinding in a porcelain mortar.

¹ Mucilage can also be advantageously employed for this work.

Under the pressure of the pestle the gold very soon resumes its natural lustre, and the grinding need not be continued further than is necessary to produce a thorough admixture of the gold with the gum. It is important that the mixture should be spread on the mussel shell without delay, since, if left to stand, the gold, by reason of its great density, will quickly settle down out of the gum.

Mussel Silver.

Like mussel gold, mussel silver can be prepared by rubbing the leaf metal down along with gum solution on a muller, and the operation may also be rendered easier by reducing the metal to an extremely fine state of division by chemical means.

With this object, silver is dissolved in nitric acid, which must, however, be perfectly free from hydrochloric acid, or the insoluble chloride of silver will be produced. During the process of solution brown fumes, possessing a suffocating odour, are given off, and as these are capable of strongly attacking the respiratory organs, the operation must be performed in the open or under a chimney with a strong draught. The silver solution, generally coloured blue from the presence of copper, is diluted with a large amount of distilled water, and a piece of sheet copper is moved quickly back and forth in the liquid. The silver separates out as a dark-grey powder, which, when washed, consists of the chemically pure metal. The silver obtained in this way may be rubbed down along with a solution of gum, and pure mussel silver will then be obtained.

Only dull gold ornamentation is obtained by the use of mussel gold. The so-called lustre gilding—the secret of which was for a long time in the sole possession of the Meissen Porcelain Works—was made more widely known by the

brothers Dutertre of Paris, who patented a process of this nature. Thirty-two grams of gold are dissolved in 128 grams of nitric acid and the same quantity of hydrochloric acid at a moderately warm temperature. Then 0.12 gram of tin and 0.12 gram of butter of antimony are added to the solution, which, as soon as they are dissolved, is diluted with 500 grams of water. Furthermore, sixteen grams of sulphur are warmed with sixteen grams of Venice turpentine and eighty grams of oil of turpentine, fifty grams of oil of lavender being added when solution is complete. An essential condition for the success of the operation is that all the materials, such as sulphur, turpentine, etc., requisite for the process shall be perfectly dry at the outset, otherwise the greater part of the dissolved sulphur will separate out again on cooling, and the sulphur balsam will be unusable. The two liquids are now poured together, warmed on the water bath and beaten until the gold is taken up by the sulphur balsam, whereby a thick olive-green mass is formed, which, after the removal of the acid water, is repeatedly washed with warm water and dried by moderate warmth. Then follows an addition of five grams of basic bismuth nitrate and 100 grams of ordinary thick oil of turpentine, after which the whole is dissolved in eighty-five grams of oil of lavender, and the lustre gold is ready for use. The mass is always warmed a little before application, so that it becomes rather more liquid; the temperature employed for firing should not be too high.

PLATINUM.

A very finely divided platinum powder is obtained by adding a solution of ammonium chloride to a solution of platinum in aqua regia, the platinum being thrown down as ammonium platino-chloride. This yellow salt is then heated to redness in an earthenware crucible until no more fumes

are evolved. The residue is a spongy, very porous, loosely coherent mass, the so-called spongy platinum. If the double salt be previously finely ground along with sea salt, and the salt afterwards extracted by water, the platinum will be obtained in a still more finely pulverised state.

Mussel platinum is prepared in a manner similar to mussel gold, and gives a fairly powerful and unchangeable metal lustre.

For the various other methods of gilding and silvering see chapter ix.

CHAPTER III.

FLUXES.

IN the introduction reference was made to the fluxes employed in both glass and porcelain painting for the purpose of fixing the colouring matter on to the article to be decorated. Only very few colours are capable of combining with the surface of glass at the temperature of fusion without any further preliminary treatment, and these merely effect a kind of cementing in colour. Others, on account of their nature, can only be made to combine with the glass surface by application in a fused condition, *i.e.*, as a thin layer of coloured glass attached by fusion. This combination is effected by means of fluxes, fusing at a lower temperature than the foundation of glass or porcelain.

There are two methods of employing these fluxes. Some few colours are simply mixed with the flux before being applied to the foundation, the combination of flux, oxide and glass surface being then effected by the temperature of fusion. On the other hand many other colours need to be first chemically combined with the flux by a preliminary fusion, the coloured flux being then employed in a powdered state for colouring the glass. This procedure is rendered necessary by the refractory nature of certain of the pigmentary oxides, which require, for their combination with the flux and for the attainment of the desired shade, a greater degree of heat than can be employed without risk for firing the colour on to the foundation.

That the constitution of the fluxes must vary fundamentally will be apparent when it is considered that different colours require different temperatures for their fusion, and when the firing temperatures, and finally the reactions of the various substances composing the finished colours, are borne in mind.

The fluxes are, for the most part, colourless vitrifiable substances, ordinarily silicates, borates or boro-silicates in various degrees of association and saturation. The materials employed in the composition of the fluxes are: felspar, quartz or sand, saltpetre, borax and boracic acid, the carbonates of potassium and sodium, minium (litharge) and bismuth oxide.

The proportion of these materials to be employed varies according to the degree of fusibility to be produced; as a rule, the variety is not so great as one might be inclined to suppose, and, in practice, certain fluxes are always used for certain colours, so that the fluxes are fewer in number than the colours themselves.

An essential condition with regard to these fluxes is that they must always be much more fusible than the glass which is to be coloured. Care is, however, necessary that the fusing points of the two shall not exhibit too great a divergence, otherwise the expansion of the glass will not coincide with that of the flux, and the whole of the colour will splinter off in scales. Mention must also be made of the attention to be directed to those reactions of borax and of silica which tend to retard the development of certain colours.

Before proceeding to the description of the fluxes themselves, the materials of which they are composed will be briefly discussed.

Felspar.

This important substance occurs in two varieties, *viz.*: orthoclase or potash felspar and albite or soda felspar—the

latter being but seldom used. In chemical composition felspar is a double silicate of alumina and an alkali, more or less contaminated with iron; lime, magnesia, etc. Pure felspar is met with only in primeval rocks, particularly, and indeed almost exclusively, in granite *in situ*. The mineralogical characteristics of felspar are: foliated structure with incomplete cleavage, *i.e.*, the foliæ are divisible on four surfaces (perpendicular to each other) of a prism, and are lustrous on those sides, but are not so on the other two sides. It has a specific gravity of 2.5, may be scratched by quartz, and is itself capable of scratching marble. In the porcelain kiln felspar fuses to a milky glass.

Quartz.

Quartz, which consists chemically of pure silica, is one of the most important materials for the preparation of fluxes, silica forming the basis of all the bodies we include under the name glass. It is, therefore, important to deal with the nature of this body rather more completely.

Quartz occurs in nature in the form of rock, quartz sand, and pebbles (flint and flint stones). Rock crystal, the purest variety of quartz, which is water-white and as transparent as glass itself, is alone suitable for the preparation of glass fluxes without any previous treatment; in the majority of cases it is imperatively necessary to subject the quartz to a process of purification, which will be described below.

Chemically, silica consists of silicon and oxygen. It occurs in two modifications, *viz.*: the crystalline, found in an almost pure condition as rock crystal and quartz, and the non-crystalline, as in flint stones and opal.

Silica belongs to the bodies which are completely infusible when heated alone in a furnace. Towards other substances it is totally inert, and may be treated with the strongest acids

without becoming attacked thereby. Only two bodies are capable of acting upon it with ease—hydrochloric acid and alkalis. When quartz is heated with caustic potash or soda, silica is dissolved in considerable quantity at boiling temperature; on being fused with soda, potash, or an alkaline earth (lime), silica combines readily with these substances to form more or less refractory compounds (silicates), and it is on this property that the manufacture of glass and enamel is based.

At ordinary temperatures silica (silicic acid) is so faintly acid that it is displaced from its soluble combinations even by carbonic acid. Solutions of waterglass (sodium silicate) rapidly set to a gelatinous mass on exposure to air, by the separation of a bulky mass of soluble silica (silica in combination with water) through the agency of atmospheric carbonic acid.

Notwithstanding this weakness at ordinary temperatures, silica acts—owing to its absolute non-volatility—at high temperatures as the strongest acid known, displacing at a strong red heat sulphuric and even phosphoric acid from their combinations. This property is frequently made use of in the manufacture of glass by employing the sulphates of the alkalis instead of the alkalis themselves.

Quartz, quartz sand and flint are the chief varieties of silica concerned in the manufacture of glass and enamels. When perfectly transparent colourless quartz (rock crystal) is at disposal, this is to be preferred; as a rule, however, rock crystal is too expensive to allow its employment in the manufacture of glass or ordinary enamel to be thought of. Nevertheless, when small quantities of fine enamel are in question, especially such as require to be very delicate in colour, rock crystal should always be used since it facilitates the working of the process considerably.

The quartz sand found in immense deposits in many places, *e.g.*, on the banks of large rivers, has usually origin-

ated in quartz-bearing rocks which have been broken down and transported by the power of water. When the sand is pure white it mostly results from the attrition of quartz rock itself, and then forms an exceptionally good material for the preparation of enamel and fine white glass, and requires but a very slight preliminary preparation in order to fit it for use. Quartz sand, resulting from the disintegration of granite or gneiss, generally contains small quantities of the minerals associated with it in the rock, these minerals being felspar and mica. The felspar is in the form of crystals, usually white in colour, whereas the mica occurs mostly as very small crystalline plates, green to black in colour.

The presence of these minerals in quartz sand detracts considerably from its value for use in the glass and enamel industries by, on the one hand, reducing the fusibility of the glass to a large extent; on the other hand, the mica colours the glass mass considerably. The purification of quartz sand from these substances being a tedious operation, and one almost impossible to carry out on a large scale, the use of this material must be avoided for fine glass, but for ordinary grades it may be employed to advantage.

In many places fine-grained sandstones, composed almost entirely of pure quartz sand, the individual grains of which are cemented together by a comparatively small amount of lime, are met with. Sandstones of this kind may be advantageously used as sources of silica for glass making after a preliminary treatment, having as its object the removal of the lime.

The so-called "infusorial earth" is a particularly valuable raw material for enamels and glass. It is a light, almost pure white mass, so loose that it may be rubbed down between the fingers to a soft, almost impalpable, powder. Microscopic examination shows this mass—erroneously termed infusorial earth—to consist of the siliceous envelope of dia-

toms, polythalamia and other low organisms, the organic matter of which has disappeared, leaving behind only the external shell, consisting almost exclusively of pure silica.

Infusorial earth can only, with difficulty, be employed for the purpose of glass making on the large scale, its bulk being so great as to give rise to difficulties in connection with its insertion in the crucibles. These difficulties are not, however, apparent in the preparation of fine enamels, and the use of this material is highly recommendable for that purpose.

Several of the varieties of quartz sand and quartz would be suitable for glass making were it not for the proportion of iron compounds they contain, which would strongly colour the glass made therefrom. In many instances, however, this inconvenience may be obviated by the method described below. A very simple test for determining whether any given quartz material is suitable for glass making direct, or will require previous purification, consists in exposing a fragment of the substance to strong red heat, and, after cooling, comparing its colour with the original. If it has not changed colour or has merely assumed a yellowish tinge, it is either entirely free from ferric oxide or contains such a small quantity as will not produce any ill effect; but if the colour changes to a decided red, this appearance indicates the presence of much ferric oxide, and such quartz is either only fit for making low grade glass or will have to be purified before use.

Purifying Quartz.

This may be effected by suffusing the finely pulverised quartz with a mixture of crude hydrochloric acid and water in equal proportions and leaving them in contact for some time, the liquid being afterwards drawn off and the quartz washed several times with water. The action of the hydrochloric acid is to dissolve out the ferric oxide present, which

it will do, provided the quartz has not previously been strongly heated to redness ; if, however, silicates of iron are present, they are not decomposed by hydrochloric acid, and they will impart a brown coloration to the glass in the subsequent fusing.

This process of purification with hydrochloric acid being rather expensive, and occasionally, as mentioned above, unattended with the desired results, it is, therefore, not particularly to be recommended. It is more advisable, for the production of fine white or fine coloured enamels, to select the most colourless quartz available, and employ this by itself.

When it is a question of producing enamels for technical purposes, then the chief consideration is power of resistance against the action of chemicals and changes of temperature, colour being merely a secondary matter. In such event one need not lay too much stress on external appearance in selecting the quartz, since a slight yellow coloration does no harm, and will, for the most part, be masked by the white substances in the foundation. Since, however, attention is generally directed to secure as fine a white as possible in the enamel for the interior (in particular) of cooking utensils, the trouble of seeking for or obtaining from a distance a really clean quartz should not be shirked ; the increased cost will be amply repaid by the superior appearance of the enamel and by the consequently enhanced value of the object.

Sedimentation.

Washing by sedimentation is a very suitable method of freeing quartz sand from foreign admixtures, and is particularly advisable when, as not infrequently happens, the chief impurity present consists of clay. It should be remarked that the silicates of alumina form glasses of unusually high fusing point, and, therefore, they require to be got rid of,

especially in the case of sand intended for the production of enamels.

Sedimental washing is performed in a very simple apparatus, consisting of a wooden vat fitted with tap holes at different heights in the side. The vat being filled about two-thirds full with clean water, the latter is stirred to keep it in continual motion and the sand is run in. When all the sand is in the stirring is discontinued, and, after waiting a few minutes until the sand is judged to have somewhat subsided, the upper tap is opened. If clay is present in the sand, its particles will float longer than those of the quartz, and the water will run off very turbid. In this event the taps are opened successively until all the water is drawn off from the vat. The taps are then turned off and more water run into the vat, the sand again stirred up with the pole and the turbid water drawn off as before, the operation being repeated until the water runs off quite clear—thus affording a proof that all the particles of clay have been floated away.

To prevent the washed sand from contamination it is shovelled up with wooden shovels out of the vat, packed in strong linen cloths and left to dry in the air, to be afterwards stored away in well-closed wooden cases until required for use. Iron shovels should not be employed, for the reason that the very hard quartz sand wears away the iron, and even the small amount of iron thus introduced into the sand will impart a considerable degree of coloration to the glass prepared therefrom.

Quenching.

Rock crystal, quartz rock and flint stones require (before they can be employed for the manufacture of glass or enamel) to be subjected to a process of disintegration whereby they are transformed into a coarse meal, since larger grains of quartz would only with difficulty be dissolved by the glass

mass, and would be readily discernible in the finished glass. In the case of a mineral of the seventh degree of hardness, such as quartz, the comminution of large quantities would require the exertion of truly gigantic power. In order to obtain disintegration by the employment of very little force, the material is first subjected to heat, followed by rapid cooling.

When rock crystal, quartz, etc., are heated to strong redness and immediately thrown into water, the cooled pieces of stone exhibit, both on the surface and through the entire mass, innumerable small cracks. In consequence of the sudden contraction suffered by the particles of glowing mineral in contact with the water, the whole of the superficial portion of the mass contracts so rapidly that the cohesion of the particles is destroyed and innumerable fissures are produced. Through these the water penetrates into the interior of the mass, and, there coming in contact with the still glowing material, is converted into steam, which, by its expansion, forces the particles of quartz asunder.

This process of suddenly cooling a glowing mineral is known in practice as "quenching". If "quenched" quartz be struck with a hammer it will break into small fragments, which can easily become converted into a fine powder.

Borax.

Borax, or the boracic acid contained therein, is frequently employed in the preparation of fluxes. There are two kinds of borax—the natural and the artificial. The former is obtained almost entirely from India and China, and is impure, on which account it has to be treated for the removal of the strongly adherent fatty impurities.

Artificial borax, which is now almost exclusively made in France and England, has nearly suppressed the natural product. There are two allotropic forms of borax, *viz.*: the

prismatic and octahedral, differing in their crystalline structure and water of crystallisation.

Prismatic borax, 47°/o water, 36·6°/o boracic acid.

Octahedral borax, 30·6°/o water, 47·04°/o boracic acid.

The crystals are colourless and are soluble in twelve parts of cold or two parts of boiling water; they have a sweet astringent taste and faintly alkaline reaction. They part with water on heating, and are converted into a frothy white mass, "calcined" borax. At higher temperatures fusion occurs, and, on cooling, the mass sets to a hard, colourless glass, which possesses, in the fused state, the property of dissolving many of the metallic oxides, whereby it becomes tinged with various colours.

Boracic Acid.

only ? This acid, a compound of boron and oxygen, forms iridescent, pliable, crystalline scales, fatty to the touch, which dissolve in twenty-five parts of cold or three of hot water. When heated to 100° C., boracic acid loses a molecule of water, and is converted into a puffy white mass; and if the heating be continued, still further fusion occurs, and boracic anhydride (vitrified borax) is formed.

Potassium and Sodium Carbonates.

These substances are too well known to need more than brief mention. The soda used for glass fluxes must be entirely free from compounds of iron, otherwise the colour of the glass will be greatly affected by the tinge due to the ferric oxide. Such a soda, perfectly free from iron, can be obtained in commerce at a price slightly in excess of that of the ordinary quality. This "enamel soda," as it is called, is especially adapted for the manufacture of coloured fluxes, and it will be readily understood that only this kind should be employed.

Similarly, it is essential that the potassium carbonate

(potash) used must be free from compounds of iron and manganese.

In place of minium, litharge carefully freed from dust may be employed in the preparation of fluxes.

The composition of the fluxes varies according to the material to which they are to be applied, the chief varieties being for :—

- (a) Glass painting.
- (b) Porcelain, earthenware and faience.

The so-called *Rocaille flux* is the only one used both for porcelain and glass painting (in addition to its employment for preparing other fluxes), and its constitution will, therefore, be enlarged upon now, leaving the other fluxes to be dealt with later on in their proper order.

Rocaille Flux.

One hundred parts quartz sand (or, failing this, calcined flint) and 300 parts minium (or litharge) are rubbed down intimately together on a glass plate, fused in a glazed crucible, and quenched by dropping the molten material into a beaker of water. The sudden cooling thereby effected divides the glass into small fragments and facilitates the subsequent grinding. Salvétat and the celebrated Brongniart do not hold with this practice of quenching the flux, since some portion thereby becomes dissolved, and the constitution of the flux therefore undergoes alteration; nevertheless, the operation is generally in vogue.

According to Salvétat, *Rocaille flux* (lead silicate) has the following average composition :—

Lead oxide	-	-	-	-	-	74.60
Silica	-	-	-	-	-	25.40
						100.00

A warning is necessary against subjecting the flux to an excessively long exposure to red heat, as it will then part with lead oxide and consequently become harder.

CHAPTER IV.

PREPARATION OF THE COLOURS FOR GLASS PAINTING.

1. BLACK.

1. *Ebony Black* :—

Iridium oxide	1½ per cent.
Flux A	3 „

The substances are simply mixed and finally ground.

2. *Deep Black* :—

Cupric oxide	2 per cent.
Flux B	1 „

3. *Dark Brown Black* :—

Cupric oxide	2½ per cent.
Flux B	1½ „
Ferric oxide	¼ „

In both cases fine grinding and proper mixing are sufficient.

4. *Dark Brown Black (Soft)* :—

Ferric oxide for black	1½ per cent.
Manganese oxide	2 „
Flux D	5½ „

Prepared as above.

5. *Fine Black* :—

Cobalt oxide	1½ per cent.
Manganese oxide	1 „
Copper scale	1 „
Iron scale	1 „

Mixed together and heated gradually till fused, whereupon the mass is at once thrown into cold water, finely powdered, mixed with Rocaille flux, 12 per cent., and ground down fine.

6. *Black* :—

Ferrous oxide	-	-	-	-	2½ per cent.
Flux C	-	-	-	-	3 „

Treatment same as No. 1.

7. *Blue Black* :—

Cobalt oxide	-	-	-	-	2½ per cent.
Litharge	-	-	-	-	$\frac{3}{4}$ „
Borax	-	-	-	-	1¾ „
Ferric oxide for black	-	-	-	-	1¼ „
Zinc oxide	-	-	-	-	$\frac{3}{4}$ „
Flux G	-	-	-	-	$\frac{3}{4}$ „
Rocaille flux	-	-	-	-	1¼ „

The cobalt oxide is ground fine; then all the materials, with the exception of the flux, are mixed together, heated to redness until fused, and then finely ground, the flux being added subsequently. With the quantities named, a fine lustrous black is produced; but if the flux be omitted or used in smaller quantity, the black will be dull instead of lustrous.

8. *Black* :—

Ferric oxide for black	-	-	-	1 per cent.
Cuprous oxide	-	-	-	1 „
Flux C	-	-	-	2½ „

Preparation same as No. 1.

9. *Antimony Black* :—

Iron scale	-	-	-	-	1½ per cent.
Cupric oxide	-	-	-	-	4½ „
Antimony oxide	-	-	-	-	6 „
Flux H	-	-	-	-	4½ „

Proceed as with No. 5.

10. *Dull Black* :—

Two recipes are employed for this black, that in which purple is used being, of course, the more expensive.

(a) *With Purple.*

Purple	-	-	-	-	1 per cent.
Cobalt oxide	-	-	-	-	1 „
Manganese oxide	-	-	-	-	1 „

Finely ground and mixed; no flux.

(b) With Copper Smalt.

Copper smalt	-	-	-	-	-	1 per cent.
Manganese oxide	-	-	-	-	-	1 „

Proceed as above; in place of manganese, the same weight of not too strongly calcined antimony may be used.

11. *Mercury Black* :—

Mercury sulphide	-	-	-	-	-	6 per cent.
Cobalt oxide	-	-	-	-	-	3 „
Cupric oxide	-	-	-	-	-	1½ „
Flux I	-	-	-	-	-	14 „

Mix the whole together and grind down fine. The mercury sulphide is prepared by grinding together four parts of mercury and four parts of sulphur in a porcelain mortar until fine, and heating the mixture to redness in a well-luted crucible. The temperature at which this heating is effected has an important influence on the product; if too low the colour will be greyish, and if too high it will turn out reddish.

12. *Hard Black* :—

Cobalt oxide	-	-	-	-	-	3 per cent.
Iron scale	-	-	-	-	-	3 „
Purple	-	-	-	-	-	1 „
Antimony oxide	-	-	-	-	-	6 „
Copper smalt	-	-	-	-	-	3 „

Treat as with No. 9, and then add

Flux H	-	-	-	-	-	3 per cent.
--------	---	---	---	---	---	-------------

13. *Hard Black, without Purple* :—

Cobalt oxide	-	-	-	-	-	6 per cent.
Cupric oxide	-	-	-	-	-	6 „
Iron scale	-	-	-	-	-	5½ „
Antimony oxide	-	-	-	-	-	8½ „
Flux H	-	-	-	-	-	4 „

As No. 12.

14. *Blackish Grey (Opaque)* :—

Cobalt oxide	-	-	-	-	-	1½ per cent.
Zinc oxide	-	-	-	-	-	3 „
Ferric oxide for black	-	-	-	-	-	1½ „
Tin oxide	-	-	-	-	-	$\frac{3}{4}$ „
Flux K	-	-	-	-	-	12 „

The whole of the ingredients are finely ground, well mixed and fused at a white heat.

15. *Blackish Grey (Opaque, Greenish):—*

Ferric oxide for black	-	-	-	-	1½ per cent.
Antimony oxide	-	-	-	-	2½ „
Zinc oxide	-	-	-	-	7 „
Tin oxide	-	-	-	-	3½ „
Cobalt oxide	-	-	-	-	2 „
Flux K	-	-	-	-	20 „

Merely requires to be finely ground and well mixed.

Some glass painters prepare special greyish-black fluxes for blacks and greys, which are mixed with the colours—according as they are desired harder or softer—and finely ground down. Similar fluxes can be employed for all tints, with corresponding care. The two recipes subjoined will amply suffice, so far as these coloured fluxes are concerned.

Flux for Black.

Cobalt oxide	-	-	-	-	1 per cent.
Quartz sand	-	-	-	-	5 „
Litharge	-	-	-	-	18 „
Borax	-	-	-	-	2 „

Fused, poured out on an iron plate and finely ground; then mixed with the black colour.

Flux for Grey.

Cobalt oxide	-	-	-	-	$\frac{3}{4}$ per cent.
Cupric oxide	-	-	-	-	$\frac{1}{8}$ „
Antimony oxide	-	-	-	-	$\frac{1}{8}$ „
Tin oxide	-	-	-	-	$\frac{3}{4}$ „
Zinc oxide	-	-	-	-	11¼ „
Borax	-	-	-	-	2½ „
Litharge	-	-	-	-	11 „
Quartz sand	-	-	-	-	4 „
Rocaille flux	-	-	-	-	1½ „

Fused at white heat, ground and stored for use.

2. WHITE.

White colour is only used for certain purposes and for producing particular effects in painting, and is then always opaque.

1. *Ordinary White* :—

Tin oxide	-	-	-	-	-	1½ per cent.
Rocaille flux	-	-	-	-	-	3 „

Finely ground on a glass plate and mixed.

2. *White* :—

Calcined bones	-	-	-	-	-	1 per cent.
Rocaille flux	-	-	-	-	-	2 „

Treated like the foregoing.

3. *White (Hard, for Vestments)* :—

Tin oxide (uncalcined)	-	-	-	-	-	2 per cent.
Quartz sand	-	-	-	-	-	1½ „
Litharge	-	-	-	-	-	2 „
Borax	-	-	-	-	-	1 „

Well mixed and heated in the fire till fused, then poured into cold water and ground. Thereafter mixed with

Rocaille flux	-	-	-	-	-	1½ per cent.
---------------	---	---	---	---	---	--------------

and finely ground.

4. *White* :—

White enamel	-	-	-	-	-	3 per cent.
Quartz	-	-	-	-	-	1 „
Fused borax	-	-	-	-	-	1½ „

Well mixed and thoroughly ground.

5. *White (Soft)* :—

White enamel	-	-	-	-	-	3 per cent.
Quartz sand	-	-	-	-	-	3½ „
Litharge	-	-	-	-	-	4 „
Antimony oxide	-	-	-	-	-	1½ „
White No. 1	-	-	-	-	-	1½ „

Fused together at red heat, thrown into water, pulverised and finely ground along with

Flux E	-	-	-	-	-	2 per cent.
--------	---	---	---	---	---	-------------

6. *White (Yellowish, Opaque)* :—

White No. 4	-	-	-	-	-	6 per cent.
Antimony oxide	-	-	-	-	-	6 „
Flux E	-	-	-	-	-	12 „

Mixed and finely ground.

7. *Covering White (according to Ami):—*

Tin oxide	-	-	-	-	7 per cent.
Fused borax	-	-	-	-	7 „
Arsenious acid	-	-	-	-	2 „
Crystal glass	-	-	-	-	34 „

The crystal glass is made by fusing together

Quartz	-	-	-	-	45 per cent.
Minium	-	-	-	-	37 „
Potassium carbonate	-	-	-	-	18 „

This white is suitable for depicting the white portions of linen cloth, white flowers, etc.; it may also be employed in painting, for overlaying white objects, with a semi-transparent coating—inducing a uniform refraction of the light, but having a solid white appearance—on the back of the glass. It should, therefore, not be used where the picture is to have a soft white tone, but only where bright white effects and tints are required.

8. *Chinese White :—*

Quartz sand	-	-	-	-	14 per cent.
White enamel	-	-	-	-	6½ „
Potassium carbonate	-	-	-	-	5½ „
Rocaille flux	-	-	-	-	12 „

Well incorporated by grinding together and stored in glass bottles. Used for mixing with other colours.

3. RED.

The most important preparation for the production of red is undoubtedly gold purple. Ferric oxide and hæmatite are also used for glass reds, but these are not so lustrous as the former, which is generally known as “gold colour”.

1. *Light Red :—*

Ferric oxide for red	-	-	-	-	2 per cent.
Antimony oxide	-	-	-	-	$\frac{1}{8}$ „
Flux D	-	-	-	-	4 „

Are mixed together, ground about half fine, and lightly roasted; then ground down fine on a glass plate.

2. *Pale Flesh Red* :—

Ferrous sulphate	-	-	-	-	2 per cent.
Alum	-	-	-	-	2 „

Crushed to coarse powder and heated in a crucible, the temperature being raised until the mixture has assumed the proper tint. The residue is then carefully extracted several times with hot water, mixed with two and a half per cent. of the subjoined flux and ground perfectly fine.

The requisite flux is prepared from :—

Flint stone	-	-	-	-	6 per cent.
Lead oxide (yellow)	-	-	-	-	4½ „
Calcined borax	-	-	-	-	1 „
Saltpetre	-	-	-	-	1 „

All finely powdered and intimately mixed in a porcelain mortar, then placed in a Hessian crucible (previously heated to redness) and kept stirred by means of a glass rod until fused to a thin fluid mass. This is poured into water, dried, powdered and bolted through a fine sieve.

3. *Light Red, with Iron* :—

Ferric oxide for red	-	-	-	1 per cent.
Flux F	-	-	-	3 „

Ground down together.

4. *Light Iron Red* :—

The following flux is first made ready by fusing together

Borax	-	-	-	-	4 per cent.
Quartz sand	-	-	-	-	4 „
Litharge	-	-	-	-	16 „
Silver chloride	-	-	-	-	2 „

and grinding down fine. Then

Flux (as above)	-	-	-	2 per cent.
Ferric oxide for red	-	-	-	5 „
Rocaille flux	-	-	-	10 „

are ground together and stored for use.

An excess of flux makes the red darker.

5. *Red* :—

Manganese oxide	-	-	-	-	2½ per cent.
Flux	-	-	-	-	20 „

Fused together until the mixture, when stirred with a glass rod, spins fine, clean threads. The molten mass is then cast into water as usual, stamped to powder and finely ground on a glass plate.

The flux consists of :—

Flint	-	-	-	-	3 per cent.
Minium	-	-	-	-	9 „

pulverised together and fused in a Hessian crucible over a progressively increasing fire; then poured into an iron mortar, crushed fine when cold and washed with water by sedimentation.

6. *Red* :—

Antimony oxide	-	-	-	-	3 per cent.
Iron ochre	-	-	-	-	2 „
Yellow lead oxide	-	-	-	-	2½ „
Copper sulphide	-	-	-	-	3 „
Silver sulphide	-	-	-	-	3 „

Finely ground in water and used immediately, without flux.

7. *Silver Red* :—

Red antimony oxide	-	-	-	-	4 per cent.
Sulphur	-	-	-	-	2 „
Silver	-	-	-	-	2 „

Heated in a crucible until fused, then poured out and finely ground. Mixed before use with

Flux (from No. 5)	-	-	-	-	4 per cent.
-------------------	---	---	---	---	-------------

and ground once more.

8. *Carmine Red* :—

Ferric oxide	-	-	-	-	3 per cent.
Flux E	-	-	-	-	7½ „

Finely ground together.

9. *Pompadour Red* :—

Ferric oxide	-	-	-	-	-	1½ per cent.
Calcined hæmatite ¹	-	-	-	-	-	½ „
Flux E	-	-	-	-	-	2 „
Flux H	-	-	-	-	-	2 „
Purple	-	-	-	-	-	¼ „

Finely ground and well incorporated.

10. *Full Red* :—²

Ferric oxide for red	-	-	-	-	-	3 per cent.
Minium	-	-	-	-	-	1½ „
Gum	-	-	-	-	-	1½ „
Lead glass	-	-	-	-	-	1½ „
Red chalk	-	-	-	-	-	9 „

The lead glass and, afterwards, the minium, gum and ferric oxide, are very finely ground on a glass plate, mixed together and then incorporated with the finely powdered red chalk, the whole being ground once again and mixed to a syrup with hot water. The liquid is transferred to a tall glass, which, to prevent access of dust, is covered over with a bell glass, on the sides of which the evaporated liquid condenses and falls down. After standing for three days all the thick matter will have subsided gently to the bottom of the glass, and the liquid shows itself at the upper edge, in transparent rings, as a fine red colour. It is now carefully decanted, and the treatment is repeated until, by several decantations, all the colour is separated from the sediment. The resulting liquids are united and evaporated to dryness in a porcelain basin at a moderate warmth—preferably by the sun—the residue being stored. The colour is always more brilliant and pure when used still moist than if thoroughly dried; if the latter condition is attained the colour should not be ground, since its transparency and beauty will be thereby diminished.

¹ Hæmatite, or red ironstone, is a dense, hard, ferruginous ore, of blood-red or brown-red colour; when pulverised and spread out it is blood-red, and the more perfect the grinding the finer the colour.

² According to Dr. Geffert.

11. *Orange Red (Hard)* :—

Yellow ferric oxide	-	-	-	-	1½ per cent.
Ferric oxide for red	-	-	-	-	3 „
Antimony oxide	-	-	-	-	¾ „
Rocaille flux	-	-	-	-	7½ „

Are gently calcined together and finely ground.

12. *Brick Red* :—

Yellow ochre	-	-	-	-	6 per cent.
Ferric oxide	-	-	-	-	¾ „
Flux E	-	-	-	-	2¾ „

Are well mixed and finely ground.

13. *Dark Carmoisin* :—

Quartz sand	-	-	-	-	1 per cent.
Minium	-	-	-	-	2 „

Calcined together, mixed with

Prepared hæmatite	-	-	-	-	1 per cent.
-------------------	---	---	---	---	-------------

and finely ground on a glass plate.

14. *Fine Red* :—

Iron saffron	-	-	-	-	1 per cent.
Rocaille flux	-	-	-	-	1 „

Mixed and finely ground. The preparation of the iron saffron requires care, the colour being fleeting; to fix it, it is generally roasted with white sea salt, the product being then powdered in a mortar till quite fine, and washed by sedimentation three or four times with hot water in order to extract the salt completely.

We come now to the “gold colours,” and have in this connection to refer once more to the preparation of gold purple.

15. *Red* :—

Gold purple	-	-	-	-	1 per cent.
Flux L	-	-	-	-	4 „

It is advisable to repeat that the shade of the gold reds depends solely on the preparation of the gold purple. According to the larger or smaller proportion of the admixed tin and

the higher or lower stage of oxidation attained by the solution, so will either beautiful red colours of various shades, such as ponceau, carmoisin, rose, etc., or only violets or even browns be produced.

16. *Purple Red* :—

Gold purple precipitate	-	-	-	1 per cent.
Flux (see below)	-	-	-	9 „

Mixed and finely ground.

The flux is made from :—

Purest flint	-	-	-	-	3 per cent.
Fused borax	-	-	-	-	8 „
Litharge	-	-	-	-	1 „
Silver chloride	-	-	-	-	$\frac{1}{8}$ „

In spite of the best recipes, it is often a very difficult matter to produce a handsome purple red, since so much depends on the variable constitution of the fluxes employed. It is highly advisable never to use the purple colours direct, but to first test the applicability of the colour, which may be easily accomplished by distributing a little of the sample on a piece of double glass and exposing it to red heat in a smelting crucible. On holding the cooled glass up to the light it will be at once apparent whether the colour is all right. If the purple is yellowish red and not nicely vitrified, this indicates an insufficiency of flux, and the purple may then be improved by adding more.

17. *Brilliant. Light Red Purple* :—

Dr. Fuchs' (dry) purple	-	-	-	1 per cent.
-------------------------	---	---	---	-------------

is ground down fine with

Flux (see below)	-	-	-	-	11 per cent.
------------------	---	---	---	---	--------------

and afterwards mixed and reground with antimony oxide one-eighth per cent. The flux is composed of

Calcined borax	■	■	■	-	7 per cent.
Quartz sand	-	-	-	-	3 „
Litharge	-	-	-	-	1 „

Fused together.

18. *English Carmine Red*:—

Salvétat's purple	-	-	-	-	1 per cent.
Flux (as below)	-	-	-	-	8 „

Mixed and ground. The flux consists of

Quartz sand	-	■	-	-	4 per cent.
Borax	-	-	-	-	3 „
Minium	-	-	-	-	3 „

Mixed together and fused.

19. *English Purple*:—

Fused borax	-	-	-	-	3 per cent.
Litharge	-	-	-	-	$\frac{1}{2}$ „
Quartz sand	-	-	-	-	1 „

Are mixed and fused, the mass being thereafter pulverised, ground fine and mixed with

Dry purple	-	-	-	-	$\frac{1}{4}$ per cent.
------------	---	---	---	---	-------------------------

4. YELLOW.

The chemical preparations employed in the production of yellow colours for glass painting have already been exhaustively described. The substances chiefly used are: antimony oxide, silver oxide, ochre and uranium oxide; the latter produces very fine yellow tints, but, unfortunately, cannot be mixed with other pigments, and is, therefore, only suitable for ground work. Yellow shades approximating to Naples yellow can be prepared from potassium antimoniate and lead oxide, and yellow may be also suitably toned by the addition of zinc, tin or ferric oxide. Lead chromate gives yellow orange, but the colour is difficult to produce, and is, moreover, unsuitable for mixing. The yellows prepared from antimony oxide are always opaque; reddish yellows are produced

by ferric, zinc and antimony oxides, and very dark yellow tones are obtainable by the aid of barium chromate.

1. *Light Yellow* :—

Pure silver (fine clippings)	-	-	2 per cent.
Crude antimony	-	-	2 „
Powdered sulphur	-	-	2 „

The antimony and sulphur are spread over the bottom of a Hessian crucible, then covered with a layer of finely clipped silver, followed by another layer, of antimony and sulphur, and so on until the whole charge is inserted. The crucible is now placed in a fire of glowing coals and covered over with fresh coal. The fusion of the mass is recognised by the spontaneous ignition of the sulphur. The whole is then poured into cold water, dried, mixed with

Dark burnt ochre	-	-	-	1 per cent.
------------------	---	---	---	-------------

and finely ground. No flux is used with this preparation. A full yellow is obtained by using three per cent. of ochre in place of the above-named quantity.

2. *Light Yellow* :—

Fine burnt ochre	-	-	-	8 per cent.
Silver chloride	-	-	-	$\frac{3}{4}$ „

Finely ground in water and stored in glass bottles for use.

3. *Dark Yellow* :—

Proceed as with No. 2, but with

Ochre	-	-	-	5 per cent.
Silver chloride	-	-	-	1 „

4. *Jonquil Yellow (Flux)* :—

Antimonic acid	-	-	-	1 per cent.
Tin	-	{ calcined }	-	1 „
Lead	-	{ together }	-	1 „
Sodium carbonate	-	-	-	1 „
Rocaille flux	-	-	-	24 „

Properly mixed, crushed, fused in a crucible and finely ground.

5. *Citron Yellow* :—

Silver oxide	-	-	-	-	-	1 per cent.
Antimony	-	-	-	-	-	$\frac{1}{4}$ „

Mixed with previously fused

Quartz sand	-	-	-	-	-	2 per cent.
Minium	-	-	-	-	-	6 „

in a mortar and finely ground, fused in a Hessian crucible over a strong fire and ground down fine.

6. *Dark Yellow (Transparent)* :—

Silver sulphide	-	-	-	-	-	1 per cent.
Burnt ochre	-	-	-	-	-	5 „

Finely ground on a glass plate and mixed. The occasion is opportune for remarking that many glass painters bestow too little attention on the difference between silver sulphide and silver chloride. It may be generally adopted as an axiom that silver sulphide is better adapted for dark yellow colours, whereas very fine medium and light shades are produced with ease by means of the chloride. All the silver colours are used without fluxes, because the use of silver oxide effects at high temperatures an actual etching of the glass by the vapour of silver, as is readily recognisable by the corrosion displayed by the outer surface of the glass and the penetration of the yellow for one half to three quarters of a centimetre into the substance of the glass. The silver colours must all be applied thickly and covered over (glazed) three or four times with great regularity.

7. *Yellow* :—

Powdered antimony	-	-	-	-	-	$1\frac{1}{2}$ per cent.
Saltpetre	-	-	-	-	-	3 „

Are heated to redness in a crucible, cooled down, powdered, ground and washed with boiling water. The resulting white is mixed with

Potassium antimoniate	-	-	-	-	-	2 per cent.
Litharge	-	-	-	-	-	$3\frac{1}{2}$ „

and ground down fine. This recipe—although the operation is rather tedious—gives the best and most certain results. The following method is easier but not quite so reliable :—

8. *Yellow* :—

Two per cent. of very dark commercial Naples yellow calcined, finely ground and mixed with two per cent. of Rocaille flux. Frequently a further addition of Rocaille flux is necessary, depending on the nature of the glass to be painted. A preliminary testing of the colour is advisable.

9. *Antimony Yellow* :—

Antimony sulphide	-	-	-	-	2 per cent.
Silver (free from copper)	-	-	-	-	1 „

Are fused together, poured into a metal mortar and pulverised on cooling. Two per cent. of this material is taken, ground very fine and mixed with six per cent. of well-burnt ochre. The shade may be varied by altering the proportion of ochre between the limits of two and eight per cent.

10. *Yellow* :—

Burnt ochre	-	-	-	-	1½ per cent.
Silver sulphide	-	-	-	-	1½ „
Antimony glass	-	-	-	-	1½ „

Pulverised as finely as possible, ground and applied to the glass direct, without any flux.

11. *Yellow* :—

Silver chloride	-	-	-	-	½ per cent.
Powdered ferruginous clay ¹	-	-	-	-	1½ „

Ground in water and applied as above.

12. *Dark Reddish Yellow* :—

Ferric oxide for red	-	-	-	-	1 per cent.
Antimony oxide	-	-	-	-	3 „

Ground together ; of this mixture two and one-quarter per cent. is taken and added to

¹ Ordinary loam.

Antimony oxide	-	-	-	-	$\frac{1}{2}$ per cent.
Flux D	-	-	-	-	6 „

The mixture is calcined at a dark red heat, and, the crucible being then removed from the fire, the mass is taken out and finely ground.

13. *Reddish Yellow* :—

Ferric oxide	-	-	-	-	1 per cent.
Antimony oxide	-	-	-	-	3 „
Flux A	-	-	-	-	10 „

Heated to faint redness and ground fine.

14. *Uranium Yellow* :—

Uranium oxide	-	-	-	-	$1\frac{1}{2}$ per cent.
Rocaille flux	-	-	-	-	6 „

Well mixed and finely ground.

15. *Uranium Yellow (Semi-transparent)* :—

Uranium oxide	-	-	-	-	1 per cent.
Flux D	-	-	-	-	$1\frac{3}{4}$ „

Fused together until a transparent glass is produced, which is then poured into cold water, ground in water and stored for use. If the colour indicates an insufficiency of flux, a further one-quarter to one-half per cent. of flux D is ground in with the colour without re-fusion.

16. *Dark Yellow, with Barium* :—

Barium chromate	-	-	-	-	$2\frac{1}{2}$ per cent.
Flux A	-	-	-	-	3 „

Are mixed and ground very fine.

17. *Yellow, with Lead Chromate* :—

Lead chrome yellow	-	-	-	-	4 per cent.
Rocaille flux	-	-	-	-	4 „

Pulverised in a mortar and inserted in a red hot Hessian crucible, the heat being continued until fusion of the mass occurs ; subsequently the material is ground down fine on a glass plate.

18. *Very Dark Yellow* :—

A flux is prepared by fusing

Quartz	-	-	-	-	-	20 per cent.
Minium	-	-	-	-	-	53 „
Fused borax	-	-	-	-	-	10 „

Mix and grind together, without fusion.

Above flux	-	-	-	-	-	6 per cent.
Zinc carbonate ¹	-	-	-	-	-	1 „
Ferric oxide ¹	-	-	-	-	-	2½ „

We come now to the orange yellow colours, of which we will treat here as an appendix to yellow. The easiest way to procure a preparation which, when fired on glass, will give an orange yellow tone, is by dissolving pure silver in chemically pure nitric acid and then reprecipitating it from the solution by means of a suspended plate of bright tin or copper. The small laminae of precipitated silver are collected, washed in warm water and finely ground. One per cent. is mixed with red No. 10, and the preparation is ready for immediate use.

19. *Orange* :—

Silver powder (as prepared above)	-	1½ per cent.
-----------------------------------	---	--------------

Mixed with

Yellow ferric oxide	-	-	-	-	1½ per cent.
Red	-	-	-	-	1½ „

and ground down very fine under water.

20. *Orange Yellow* :—

Yellow No. 8	-	-	-	-	3 per cent.
Ferric oxide	-	-	-	-	½ „
Rocaille flux	-	-	-	-	¾ „

Ground very fine, without fusion.

21. *Orange Yellow* :—

A very fine and brilliant orange yellow may be prepared

¹ In the condition of hydrate.

by means of lead chromate; but this substance is unsuitable for mixing with other colours.¹

Lead oxide	-	-	-	-	-	7½ per cent.
Minium	-	-	-	-	-	7½ „

Are mixed and fused over a brisk fire. Some quartz may be added, but very little, the silica changing the colour to yellow and greatly facilitating its alteration at a high temperature. The employment of the flux given under No. 18 is more advantageous.

22. *Orange (for Ground Work):—*

Uranium oxide	-	-	-	-	2½ per cent.
Rocaille flux	-	-	-	-	7½ „

Mixed and finely ground.

5. GREEN.

Most of the greens are prepared with cupric oxide or chromic oxide. To produce bluish-green colours in particular, cobalt oxide is frequently associated with the foregoing, whilst for yellow-green tints mixtures of yellows and blues are employed, to which we will revert in due course.

1. *Cobalt Green:—*

Dissolve—

Cobalt oxide	-	-	-	-	3 per cent. in
Nitric acid	-	-	-	-	7 „ and, on the other hand,
Tin turnings	-	-	-	-	2 „ in
Hydrochloric acid	-	-	-	-	6 „

Mix the two solutions, and precipitate with potassium carbonate. The precipitate is collected on blotting paper, well washed and dried, the mass being then heated to redness for six or eight hours. On cooling, this green is mixed with five per cent. of the following flux:—

¹ On the other hand all the antimony yellows are miscible.

Quartz sand	•	•	•	•	•	2 per cent.
Minium	-	-	-	-	-	4 „
Borax glass	-	-	-	-	-	1 „

Fused together and pulverised.

2. *Bluish Green* :—

The colour is first made ready by grinding

Chromic oxide	-	-	-	-	5 per cent.
Cobaltous carbonate	-	-	-	-	$2\frac{1}{2}$ „
Zinc bicarbonate	-	-	-	-	$2\frac{1}{2}$ „

thoroughly on a glass plate, drying and calcining for a quarter of an hour in a strong fire. Of this colour two and a half per cent. is then taken and mixed with seven and a half per cent. of flux, without fusion.

3. *Dark Blue Green* :—

Chromic oxide (freshly precipitated)	1 per cent.
Cobalt blue	$\frac{1}{2}$ „

Well ground together, calcined in a crucible at red heat, and mixed with three per cent. of the above flux.

4. *Green (Opaque)* :—

Chromic oxide	-	-	-	-	1 per cent.
Subjoined flux	-	-	-	-	$2\frac{1}{2}$ „

Mixed and finely ground without fusing. The quantitative composition of the flux is :—

Borax glass	-	-	-	-	3 per cent.
Litharge	-	-	-	-	$7\frac{1}{2}$ „
Quartz sand	-	-	-	-	$2\frac{1}{4}$ „

which, with the exception of the borax glass, must be well calcined. The borax glass is added subsequently, and the whole well ground.

The advantage of this green is that it mixes easily with other colours. By itself the colour is not very fine.

5. *Yellowish Green* :—

This colour is prepared from

Quartz sand	-	-	-	-	2½ per cent.
Litharge	-	-	-	-	6½ „
Borax glass	-	-	-	-	2½ „
Chromic oxide	-	-	-	-	1½ „
Lead chromate	-	-	-	-	1 „

The mixture is heated to strong red heat and then quenched in water.

6. *Full Green (Semi-transparent) :—*

A flux is prepared by fusing

Borax glass	▪	▪	▪	▪	5 per cent.
Minium	-	-	-	-	13 „
Silica	-	-	-	-	4½ „

On the other hand, a mixture of

Chromic oxide	-	-	-	-	3 per cent.
Silver chloride	▪	▪	▪	▪	½ „
Above flux	-	-	-	-	20 „

is made and calcined at strong red heat. The green may be rendered more transparent by the employment of a binding material similar to the Rocaille flux, to which a little silver chloride is added.

7. *Green (Flux) :—*

Green cupric carbonate	-	-	-	-	3 per cent.
White glass, in powder	-	-	-	-	12 „
Litharge	▪	▪	▪	▪	6 „

Mixed and [exposed in a glazed Hessian crucible to the strongest red heat until perfectly clear glass threads can be spun from the mass. It is then removed from the crucible by a hook, cast into water, dried and powdered.

8. *Green (Flux) :—*

This flux is particularly suitable for recipes Nos. 5 and 6.

Borax glass	-	-	-	-	1½ per cent.
Quartz sand	-	-	-	-	1 „
Minium	-	-	-	-	3 „
Silver chloride	-	-	-	-	½ „

These substances are fused until perfectly liquid, care

being necessary that no impurities get into the mass, otherwise the silver will be immediately precipitated.

Three per cent. of the above mixture is mixed and finely ground with one and a half per cent. of well-calced lead chromate. The powder is then raised to a low red heat in the fire, the mass being stirred all the time with a steel spoon to ensure thorough calcination of the whole.

9. *Flux* :—

Cupric oxide	-	-	-	-	2 per cent.
Potassium antimoniate	-	-	-	-	20 „
Flux	-	-	-	-	60 „

Well mixed, calcined and ground. The flux consists of

Quartz sand	-	-	-	-	1 per cent.
Litharge	-	-	-	-	3 „

10. *Green (Flux)* :—

Cupric borate	-	-	-	-	1½ per cent.
White glass powder	-	-	-	-	4½ „
Litharge	-	-	-	-	1½ „

Mixed and treated in the same manner as No. 7.

11. *Green (Hard)* :—

Cupric oxide	-	-	-	-	3 per cent.
Yellow antimony oxide	-	-	-	-	$\frac{3}{4}$ „
Tin oxide	-	-	-	-	$\frac{1}{8}$ „
Rocaille flux	-	-	-	-	9 „
Flux G	-	-	-	-	9 „

First coarsely powdered, ground fine under water and stored for use. This preparation always appears black, and is so applied, but it produces a very fine shade of green.

12. *Green* :—

Chromic oxide	-	-	-	-	2 per cent.
Rocaille flux	-	-	-	-	6 „

Finely ground, without calcination.

13. *Green (Dark)* :—

Chromic oxide	-	-	-	-	7½ per cent.
Cobalt carbonate	-	-	-	-	2½ „

Mixed, calcined and then mixed and ground with

Rocaille flux	-	-	-	-	30 per cent.
---------------	---	---	---	---	--------------

14. *Green (for Green Distances):—*

Manganese peroxide	-	-	-	-	13 per cent.
Cobalt blue	-	-	-	-	26 „

Mixed and finely ground. The following recipe is applicable to the same purpose:—

15. *Green:—*

Pure cobalt oxide	-	-	-	-	7 per cent.
Flux	-	-	-	-	3½ „

Ground down fine together.

The flux is prepared from

Quartz sand	-	-	-	-	10 per cent.
Minium	-	-	-	-	21 „

16. *Green (Brown-Green):—*

Manganese oxide	-	-	-	-	1½ per cent.
Cupric oxide	-	-	-	-	4½ „
Borax	-	-	-	-	3 „
Antimony oxide	-	-	-	-	7½ „
Minium	-	-	-	-	12 „
Cobalt blue	-	-	-	-	2 „

Fused over a strong fire, poured out, mixed with

Yellow ochre (washed by sedimentation)	-	-	-	-	3 per cent.
Yellow ferric oxide	-	-	-	-	¾ „
Iridium black	-	-	-	-	⅜ „
Rocaille flux	-	-	-	-	3 „

The whole finely ground together and stored for use.

A number of green colours for glass painting are offered for sale under various names, their composition being for the most part kept secret by the manufacturers. Of course, it is not a very difficult matter for the technical chemist, by the aid of a series of experiments, to imitate any given shade of colour.

6. VIOLET.

By repeating the original amount of tin solution as an addition to the precipitate of gold purple fine shades of violet are produced, and are, in fact, the handsomest tones obtainable in this class of colour. Shading may be effected by

means of cobalt blue, but the violet thereby loses its beauty and lustre. Black ferric oxide may be also used for violets, and though they are never so handsome as the gold violets, they are very frequently employed, being highly suitable for shadow effects and consorting well with most of the other colours. Manganese peroxide also produces violets similar in shade to those from ferric oxide.

1. *Violet (Purple) :—*

Gold purple	-	-	-	-	-	1 per cent.
Rocaille flux	-	-	-	-	-	1 "
Flux H	-	-	-	-	-	3½ "

Fused, pulverised² and ground. In this case, silver chloride³ should be omitted from the composition of the flux H.

2. *Violet (Purple) :—*

Flux (see below) ^{2,4}	-	-	-	-	-	10 per cent.
Gold purple	-	-	-	-	-	1 "

Mixed and finely ground. The flux consists of

Litharge	-	-	-	-	-	6 per cent.
Borax glass	-	-	-	-	-	2 "
Quartz sand	-	-	-	-	-	2½ "

Fused at white heat, quenched in cold water and then mixed with the gold purple in the proportion named.

3. *Violet :—*

The author has obtained a similar but livelier colour with a flux of the following composition :—

Borax glass	-	-	-	-	-	4 per cent.
Minium	-	-	-	-	-	3 "
Silica	-	-	-	-	-	2 "

nine parts of which were mixed with one part of gold purple. The method of treatment is the same as for No. 2.

4. *Purple Violet :—*

A very handsome purple violet may be prepared by grinding together

Freshly precipitated gold purple	-	-	-	-	-	1 per cent.
Rocaille flux	-	-	-	-	-	4 "

The gold purple must be mixed with the flux in a moist condition, directly after precipitation and washing, without a preliminary drying. In these preparations, more depends on the gold purple itself, *i.e.*, on the amount of tin employed in its precipitation, than on the maintenance of an exact ratio between the gold and the flux. Silver chloride, which may occur in gold purple if not prepared with scrupulous care, has a particularly unfavourable effect on the purple violet obtained.

French chemists, such as Salvétat and Brongniart, decry the action of silver chloride in the preparation of violet from gold purple, and recommend fluxes containing a large amount of lead. Dr. Geffert,¹ on the other hand, commends the use of silver chloride for the production of certain violets for glass.

Experiments made by the author in this direction show that although a violet can be produced by gold purple in presence of silver chloride, it is characterised by a shade differing from that of the ordinary violet, and that the application of silver chloride to gold purple is, as a rule, advisable only in the production of the so-called carmine colours. The recipe for preparing reddish violet with silver chloride and gold purple is given hereinafter.

This is a suitable occasion to repeat that the quantitative proportions, given for recipes wherein gold purple figures, are always defective and cannot be stated with certainty, owing to the circumstance that the gold is used *moist*; it is, therefore, only by long practice and experience that it becomes possible to gauge the correct ratio of flux and colour necessary to produce a fine and properly fusible colour. On this account it is necessary to test the colour when the materials have been ground to the requisite degree of fineness.

¹ Author of a *History of Glass Painting*.

5. *Violet. Geffert's Recipe:—*

Gold purple is mixed with various amounts of silver chloride, previously fused with ten times their own weight of a flux composed of

White quartz, washed and calcined -	3 per cent.
Calcined borax - - - - -	5 „
Minium - - - - -	1 „

The gold purple is also incorporated with this flux, and the whole ground fine. On the other hand, the precipitation of the gold purple may be effected in such a manner that it comes down along with silver chloride. To this end a little tin solution is stirred into a large volume of water, a little silver nitrate being then added and immediately followed by the gold solution. The quantitative ratio of the solutions must be ascertained by experiment. The precipitate is mixed with an equal amount, or rather more, of the following flux:—

Quartz sand - - - - -	8 per cent.
Borax glass - - - - -	4 „
Saltpetre - - - - -	1 „
White chalk - - - - -	1 „

Treated as in the case of flux F.

6. *Dark Violet:—*

Fine freshly precipitated gold purple - -	1½ per cent.
Flux - - - - -	9 „

Ground down fine together. The flux is made by fusing

Quartz sand - - - - -	2 per cent.
Minium - - - - -	4 „
Borax glass - - - - -	½ „

By employing six to eight per cent. of minium instead of four, deeper tones are produced, which, however, at the same time assume a violet-coloured wine-yeast shade, a colour which is not very handsome, although occasionally employed.

We come now to the mixtures of gold purple and cobalt blue, whereby very fine colours can be obtained. This is, indeed, the only method of mixing red and blue by which it

is possible to produce—according to the proportion of purple and pale or deep blue employed—the entire range of violet shades.

7. *Pale Violet* :—

Gold purple	-	-	-	-	-	1 per cent.
Royal smalt	-	-	-	-	-	3 „

Ground together and mixed with Rocaille flux as required.

8. *Violet* :—

Gold purple	-	-	-	-	-	1 per cent.
Cobalt blue	-	-	-	-	-	2 „
Flux H	-	-	-	-	-	1 „
Flux J	-	-	-	-	-	6 „

Well ground together without previous fusion. It is easy, even for a beginner, to prepare any desired degree of violet by varying the proportions of blue and gold purple.

9. *Violet from Manganese* :—

A mixture is prepared from

Manganese oxide	-	-	-	-	-	15 per cent.
Borax glass	-	-	-	-	-	2½ „
Saltpetre	-	-	-	-	-	60 „
Sand	-	-	-	-	-	22½ „

and of this mixture $33\frac{1}{3}$ per cent. is taken and fused with Rocaille flux $66\frac{2}{3}$ per cent.

10. *Violet (Hard)* :—

The preceding recipe was introduced by Brongniart, the director of the Sèvres Works. To produce the same shade in harder colour take

No. 9 violet	-	-	-	-	-	26 per cent.
Sand	-	-	-	-	-	26 „
Potassium carbonate	-	-	-	-	-	13 „
Saltpetre	-	-	-	-	-	6 „
Minium	-	-	-	-	-	26 „

Two layers of this colour must be applied.

11. *Violet (Medium)* :—

Manganese oxide	-	-	-	-	2 per cent.
Saltpetre	-	-	-	-	2 „

are calcined thoroughly in a pottery kiln and then mixed with

White glass powder	-	-	-	12 per cent.
Minium	-	-	-	4 „

The mixture is well fused and treated by quenching in water, pulverising and grinding as usual.

12. *Violet* :—

Manganese oxide	-	-	-	-	3 per cent.
Silica	-	-	-	-	6 „
Minium	-	-	-	-	27 „

are fused together. The shade of violet will vary with the quantitative ratio between manganese oxide and flux.

13. *Violet (Opaque)* :—

To prepare an opaque violet :—

Manganese carbonate	-	-	-	1½ per cent.
Quartz	-	-	-	10 „
Borax	-	-	-	5 „
Minium	-	-	-	20 „
Tin oxide	-	-	-	5 „

are fused together.

14. *Deep Violet* :—

Three per cent. of ferric oxide (for black), maintained at white heat for an hour, and mixed with nine per cent. of flux A, without calcining. As has already been mentioned, the violet prepared with ferric oxide is highly suitable for shading, since it agrees very well with yellow, light and dark red, black and brown.

15. *Violet* :—

A mixture of manganese and ferric oxides will also give violet. The following recipe will give the requisite indications :—

Manganese oxide	-	-	-	-	3 per cent.
Quartz sand	-	-	-	-	6 „
Litharge	-	-	-	-	36 „

Mixed, fused at a strong red heat, poured out and ground fine when cooled down. Of this

Powder	-	-	-	-	15 per cent. is mixed with
Ferric oxide (as for No. 14)	-	-	-	-	3 „
Rocaille flux	-	-	-	-	2 „

and again ground fine.

16. *Violet* :—

Manganese oxide	-	-	-	-	3 per cent.
Zaffre	-	-	-	-	3 „
White glass powder	-	-	-	-	30 „
Minium	-	-	-	-	12 „

Mixed and treated in the usual manner in a strong smelting fire.

7. BLUE.

The various compounds of cobalt form the principal materials for the production of blue for glass ; less frequently copper is employed for this purpose.

1. *Sky Blue (for Ground Work)* :—

Cobaltous carbonate	-	-	-	-	14 per cent.
Zinc bicarbonate	-	-	-	-	20 „
Flux	-	-	-	-	160 „

Are mixed and fused. The flux consists of a fused combination of

Quartz	-	-	-	-	20 per cent.
Minium	-	-	-	-	60 „
Fused borax	-	-	-	-	10 „

This flux is more or less suitable for use with all the blue colours prepared from cobalt oxide, since it contains an excess of boracic acid, and is, therefore, by reason of its acid nature, the safest to use, because cobalt oxide produces blue only when in combination as this salt, the formation of which has, therefore, to be ensured.

2. *Azure Blue (Ground)* :—

Cobalt oxide	-	-	-	-	11 per cent.
Zinc oxide	-	-	-	-	22 „
Flux from No. 1	-	-	-	-	67 „

Are mixed and fused. This very fine colour offers the advantage that it may be shaded by admixtures of grey and black.

3. *Pale Blue* :—

Best royal smalt	-	-	-	-	20 per cent.
Finely powdered white glass	-	-	-	-	20 „
Litharge	-	-	-	-	20 „

Well mixed and exposed in a glazed crucible to the strongest fire until perfectly clear azure blue threads can be spun from the mass, which is then hooked out of the crucible and quenched in cold water; when dry it is ground for use. It should be noted that the proportion of litharge must be adjusted according to the (variable) fusibility of the commercial varieties of smalt. (This holds good for all preparations of cobalt.)

4. *Pale Blue (Flux)* :—

Zaffre	-	-	-	-	10 per cent.
Finely powdered white glass	-	-	-	-	40 „
Saltpetre	-	-	-	-	30 „
Minium	-	-	-	-	30 „

Mixed, fused and ground as in the preceding recipe.

5. *Medium Blue* :—

Cobalt blue	-	-	-	-	10 per cent.
White antimony oxide	-	-	-	-	2½ „
Tin oxide	-	-	-	-	2½ „
Flux K	-	-	-	-	3 „

Simply ground together and stored for use.

6. *Turquoise Blue* :—

Pure cobalt oxide	-	-	-	-	1 per cent.
Calcined alum	-	-	-	-	40 „
Zinc oxide	-	-	-	-	¼ „

Ground extremely fine, then ground and lightly calcined with

Minium	-	-	-	-	-	24 per cent.
Borax	-	-	-	-	-	8 „
Quartz sand	-	-	-	-	-	7 „

previously fused and quenched.

7. *Turquoise Blue* :—

The following recipe, given by Robert, also yields a handsome blue :—

Cobalt oxide	-	-	-	-	-	6 per cent.
Zinc oxide	-	-	-	-	-	2 „

Dissolved in hydrochloric acid and mixed with

Alum	-	-	-	-	-	92 per cent.
------	---	---	---	---	---	--------------

which has been previously dissolved in water. The mixture is filtered, and sodium carbonate added until neutral; the resulting white precipitate is carefully cleansed by washing until neutral, finely ground and calcined in a crucible. A low red heat is employed, and afterwards raised to strong red heat, whereupon the crucible is quickly removed from the fire and set to cool. Of the resulting preparation five per cent. is mixed with previously fused and pulverised

Litharge	-	-	-	-	-	253 per cent.
Borax glass	-	-	-	-	-	300 „
Silica	-	-	-	-	-	75 „

the whole being finely ground and stored for use.

8. *Medium Blue (Flux)* :—

Cobalt oxide	-	-	-	-	-	5 per cent.
Borax glass	-	-	-	-	-	20 „

fused in a strong fire for four hours and mixed before use with a flux of

Rock crystal	-	-	-	-	-	5 per cent.
Borax glass	-	-	-	-	-	5 „

Previously crushed and fused.

9. *Medium Blue* :—

Calcined cobalt oxide	-	-	-	19 per cent.
Calcined sodium carbonate	-	-	-	39 „
Sand	-	-	-	38 „
Borax glass	-	-	-	3 „

Mixed, placed in an earthen crucible and heated for an hour in a blast furnace with a good draught; then left to cool. It is generally necessary to break up the crucible in order to get out the blue vitreous lump at the bottom, and the preparation has then to be pulverised and ground fine.

10. *Dark Blue* :—

Cobalt oxide	-	-	-	-	5 per cent.
Quartz sand	-	-	-	-	12 „
Minium	-	-	-	-	22 „
Borax	-	-	-	-	12 „

are fused together, left to cool and ground fine. It frequently happens that this blue is too soft (fusible) for the glass to which it is to be applied, a defect which manifests itself by the formation of small fissures in the glass after fusing. In such event, all that is necessary is to add a little cobalt oxide to the preparation, which is thereby rendered more refractory. Samples should then be tested until the desired hardness is attained. It often happens that the colour is, on the other hand, too hard for the glass; in that case more minium must be added.

11. *Deep Royal Blue (Salvétat's Recipe)* :—

Cobalt oxide	-	-	-	-	20 per cent.
Sand	-	-	-	-	20 „
Potassium carbonate	-	-	-	-	42 „

fused together. The resulting dark mass is pulverised, ground, mixed with fifty per cent. of Rocaille flux and re-fused.

12. *Fine Dark Blue* :—

For this the author prepares an oxide in a special manner. Well-roasted cobalt glance is left in undisturbed contact

for two or three days with nitric acid diluted with two-thirds of water. When the solution becomes gradually light and fine red in colour, it is carefully poured off so as to avoid carrying away any of the sediment. The latter is again treated several times with water and a little nitric acid in order to completely extract any red colour residual therein, and the resulting solutions are then united in a porcelain basin.

Six per cent. of this red solution is mixed with two per cent. of purified salt, and, as soon as the latter is dissolved, the liquid is poured off from the sediment—which is unfit for use—and gently warmed in a porcelain dish. During the next few hours, so often as a fresh sediment is formed by the evaporation of the liquid, the latter is again poured off carefully, but should be afterwards stirred industriously with a glass rod, especially when it begins to thicken, until finally it changes to a granular salt of a handsome blue colour. This salt is left in the warm for another hour or two, and is then exposed to the air until, in a few days, it has become carmoisin red, whereupon it is warmed up again and once more turns blue, again changing to red on exposure to the air; the treatment being repeated until the salt no longer evolves nitric acid fumes on warming. The mass is then dried in a porcelain basin over glowing coals, whereupon it finally changes to a most beautiful permanent blue. For use, one per cent. of this oxide is mixed with two and one-half per cent. of a flux consisting of

Rock crystal	-	-	-	-	-	4 per cent.
Borax glass	-	-	-	-	-	4 „

crushed together, fused, poured into water, bruised in an iron mortar and ground down fine on a glass plate.

13. *Dark Blue (Flux):—*

Finest royal smalt	-	-	-	-	-	20 per cent.
Litharge	-	-	-	-	-	12½ „

Treated in the manner described for blue No. 3.

14. *Dark Blue (Flux)* :—

Black cobalt oxide	-	-	-	-	10 per cent.
White powdered glass	-	-	-	-	20 „
Minium	-	-	-	-	20 „
Saltpêtre	-	-	-	-	20 „

Treated the same as No. 13. With these colours the greatest variety of blue shades can be easily prepared by regulating the quantitative proportions of the colour and flux.

15. *Greenish Blue (Dark)* :—

Cobalt carbonate	-	-	-	-	10 per cent.
Antimony oxide	-	-	-	-	2½ „
Cupric oxide	-	-	-	-	5 „
Zinc oxide	-	-	-	-	10 „
Flux C	-	-	-	-	100 „

Fused, poured out, crushed and finely ground.

16. *Blue (perfectly Opaque)* :—

Cobalt oxide	-	-	-	-	3 per cent.
Quartz sand	-	-	-	-	50 „
Borax	-	-	-	-	25 „
Minium	-	-	-	-	100 „
Zinc oxide	-	-	-	-	15 „

Fused together and finely ground.

17. *Blue Black (Hard)* :—

Ferric oxide for black	-	-	-	-	5 per cent.
Cobalt oxide	-	-	-	-	10 „
Dark blue No. 14	-	-	-	-	20 „
Rocaille flux	-	-	-	-	5 „

Well mixed and ground fine.

18. *Greenish Blue (Hard)* :—

Cobalt oxide	-	-	-	-	10 per cent.
Chromic oxide	-	-	-	-	20 „
Alumina	-	-	-	-	30 „

This composition gives a greenish-blue colour of a decided blue shade. By altering the ratio of cobalt and chromic oxide, any desired range of bluish or greenish shading may be obtained. It must not, however, be forgotten that the pigmentary power of cobalt oxide is much greater than that

of chromic oxide, and that, if the two be employed together in equal quantities, the blue will be nearly pure, the green tone being entirely suppressed.

19. *Blue, with Copper*:—

According to Brongniart, this colour is prepared from

Minium	-	-	-	-	-	33 per cent.
Aquamarine	-	-	-	-	-	67 „

However, since it is now rare to find a commercial aquamarine which will produce a fine rich blue when used with half its weight of minium, the preparation is, of course, abandoned.

8. BROWN.

In preparing brown colours for glass the most divergent oxides are employed in conjunction. For instance, very fine yellow-browns are obtained by simply mixing zinc oxide and ferric oxide, the resulting shade varying with the condition of the two oxides. Manganese, when used with suitable fluxes, also gives brown tones; hæmatite alone, or in combination with manganese peroxide, is also frequently used for the same purposes, and Terra di Sienna, umber, etc., are likewise employed.

1. *Yellow Brown*:—

A flux is prepared from

Quartz sand	-	-	-	-	-	20 per cent.
Litharge	-	-	-	-	-	40 „
Borax glass	-	-	-	-	-	20 „

by fusion, twenty-five per cent. being then taken and mixed with ten per cent. of yellow ferric oxide.

When the whole has been finely ground it is calcined at low red heat, and the resulting yellow-brown vitreous mass re-ground fine.

2. *Nankin Brown*:—

Yellow ferric oxide	-	-	-	-	7 per cent.
Zinc oxide	-	-	-	-	13½ „
Flux used for blue No. 1	-	-	-	-	80 „

Mixed but not fused.

3. *Ochre Brown*:—

A brown tint, analogous to the above two, but fuller, is obtained from

Yellow ferric oxide	-	-	-	-	8½ per cent.
Zinc oxide	-	-	-	-	15 „
Above flux	-	-	-	-	76½ „

Treated as for No. 2.

4. *Dark Brown Yellow*:—

Yellow ferric oxide	-	-	-	-	13 per cent.
Zinc oxide	-	-	-	-	13 „
Flux same as No. 3	-	-	-	-	74 „

Prepared as above. These recipes—Nos. 2, 3 and 4—were originated by Bunel; they produce very good results, and are also specially to be recommended because they mix well with all other colours except greens.

Bunel gives recipes for two other colours, one of which may be mixed with green without blackening or muddying chrome green. In this connection, it should be noted that the careful preparation of the zinc oxide is important, and the reader is, therefore, referred to the page (63) dealing with that operation.

5. *Ochre Brown (for Mixing with Green)*:—

Yellow ferric oxide	-	-	-	-	14½ per cent.
Zinc oxide	-	-	-	-	14½ „
Above flux	-	-	-	-	71½ „

6. *Very Dark Ochre Brown*:—

Yellow ferric oxide	-	-	-	-	23¾ per cent.
Zinc oxide	-	-	-	-	10 „
Above flux	-	-	-	-	66¼ „

In both of these recipes the colours, etc., need only be ground fine together, without fusing.

7. *Full Havanna Brown*:—

Flux as used for No. 1	-	-	-	25 per cent.
Yellow ferric oxide	-	-	-	15 „
Antimony oxide	-	-	-	1½ „
Terra di Sienna	-	-	-	1½ „

Simply ground down together.

8. *Brown (Flux)*:—

Manganese oxide	-	-	-	2 per cent.
Sand	-	-	-	8 „
Litharge	-	-	-	24 „

Well fused together, powdered and ground fine.

9. *Brown (Flux)*:—

Yellow No. 1	-	-	-	4 per cent.
Antimony	-	-	-	2 „
Borax	-	-	-	½ „
Rocaille flux	-	-	-	6 „

Fused together, pulverised and finely ground.

10. *Brown, Dark (Flux)*:—

Manganese peroxide	-	-	-	10 per cent.
Blue No. 12	-	-	-	2½ „
Rocaille flux	-	-	-	80 „

Treated like No. 9.

11. *Medium Yellow Brown*:—

Burnt yellow ochre	-	-	-	3 per cent.
Yellow ferric oxide	-	-	-	3 „
Antimony oxide	-	-	-	3 „
Flux D	-	-	-	7½ „

Ground fine together on a glass plate, without previous calcination.

12. *Sepia Brown*:—

Manganese oxide	-	-	-	10 per cent.
Yellow ferric oxide	-	-	-	30 „
Terra di Sienna	-	-	-	30 „
Antimony oxide	-	-	-	5 „
Flux D	-	-	-	150 „

Grind all the ingredients together till fine, calcine in a strong fire, leave to cool and grind fine. This brown is highly suitable for blonde hair.

13. *Medium Brown*:—

Yellow ferric oxide	-	-	-	-	4 per cent.
Manganese oxide	-	-	-	-	6 „
Yellow No. 1	-	-	-	-	6 „

Fused together, poured into water, and, after cooling, mixed with

Flux I	-	-	-	-	-	6 per cent.
--------	---	---	---	---	---	-------------

14. *Brown, with Hæmatite*:—

Hæmatite	-	-	-	-	-	10 per cent.
Manganese oxide	-	-	-	-	-	5 „
Silver-antimony sulphide	-	-	-	-	-	$\frac{1}{2}$ „

are heated to strong redness for half an hour, mixed with

Lead glass	-	-	-	-	-	16 per cent.
Gum water	-	-	-	-	-	1 „

and ground very fine with a glass muller. A fine brown is also very easily prepared by means of the sediment left behind in the preparation of the red colour from ferric oxide, which may be used without further treatment.

15. *Yellowish Brown*:—

Golden yellow No. 1	-	-	-	-	14 per cent.
Manganese oxide	-	-	-	-	2 „

are ground finely together and the preparation used just as it is, without previous calcination or flux of any kind.

16. *Brown, with Umber*:—

To produce such a brown, it is merely necessary to fuse three per cent. of calcined umber with

Flux D	-	-	-	-	-	6 per cent.
--------	---	---	---	---	---	-------------

in the fire and grind down fine when cold.

17. *Red Brown*:—

Yellow ferric oxide	-	-	-	-	3 per cent.
Manganese oxide	-	-	-	-	5 „
Zinc oxide	-	-	-	-	3 „
Flux A	-	-	-	-	30 „

18. *Brilliant Yellow Brown, with Gold Purple*:—

A well-glazed fusing crucible is heated to redness and the following mixture:—

Litharge -	-	-	-	-	3 per cent.
Rocaille flux -	-	-	-	-	3 „
Quartz sand -	-	-	-	-	6 „
Silver chloride -	-	-	-	-	1½ „

thrown in. When properly fluid it is poured into cold water, crushed, ground fine and mixed with

Gold purple -	-	-	-	-	3 per cent.
---------------	---	---	---	---	-------------

19. *Mahogany Brown*:—

Manganese oxide -	-	-	-	-	4 per cent.
Cobalt oxide -	-	-	-	-	1 „
Zinc oxide -	-	-	-	-	3 „
Yellow ferric oxide -	-	-	-	-	1 „
Flux A -	-	-	-	-	18 „
Flux K -	-	-	-	-	4 „

are ground extremely fine, without fusion. By employing a larger percentage proportion of zinc oxide, the colour—as is the case with all browns—may be lightened in shade.

20. *Brown Black*:—

Cobalt oxide -	-	-	-	-	6 per cent.
Manganese oxide -	-	-	-	-	9 „
Yellow ferric oxide -	-	-	-	-	4 „
Flux I -	-	-	-	-	39 „

Treated in the same way as No. 19.

21. *Brown, with Ferrous Chromate*:—

Ferrous chromate -	-	-	-	-	6 per cent.
Rocaille flux -	-	-	-	-	3¼ „
Flux D -	-	-	-	-	11 „

Simply ground down together, without fusion.

FLUXES.

As supplementary to the colours for glass painting, we append the various fluxes generally used, referring the reader also to what has already been mentioned in the previous

pages, and to the description of the preparation of Rocaille flux.

Flux A:—

Quartz sand	-	-	-	-	-	30 per cent.
Minium	-	-	-	-	-	80 „
Borax glass	-	-	-	-	-	10 „

The mixture is fused in a glazed crucible, the fluid mass being thrown into cold water, which is immediately poured off and the substance transferred to a filter to drain.

Flux B:—

Crystallised borax	-	-	-	-	-	10 per cent.
Litharge	-	-	-	-	-	10 „
Powdered glass	-	-	-	-	-	10 „

After mixing, these ingredients are fused (in a blast furnace) in a Hessian crucible for an hour or an hour and half, then poured into a vessel of water, dried and pulverised on a glass plate.

Flux C:—

This flux consists of

Lead glass	-	-	-	-	-	20 per cent.
Gum arabic	-	-	-	-	-	2½ „

The lead glass is ground down with water on a copper plate or an ordinary stone until sufficiently fine, the gum arabic being added only after the colouring oxides have been mixed in. The whole is then ground as fine as possible.

Flux D:—

Clean flintstone	-	-	-	-	-	20 per cent.
Lead oxide	-	-	-	-	-	60 „
Borax glass	-	-	-	-	-	15 „

Prepared like Flux A.

Flux E:—

Purified silica	-	-	-	-	-	30 per cent.
Litharge	-	-	-	-	-	70 „
Fused borax	-	-	-	-	-	10 „

are fused in a glazed crucible and then treated as for Flux D.

Flux F:—

Washed and calcined white sand	-	60 per cent.
Yellow lead oxide	- - - -	50 „
Bismuth nitrate	- - - -	30 „

Finely powdered, intimately mixed in a porcelain mortar and placed in a covered Hessian crucible, previously heated to redness, wherein they are stirred continually with a steel rod until liquid. The mass is then poured out into a vessel of water, dried, pulverised and bolted through a fine sieve. This metal flux must on no account be brought into contact with alkali carbonates, otherwise the bismuth will be precipitated.

Flux G:—

The under-mentioned substances are heated very gradually in a crucible, then poured into cold water and finally ground fine.

Quartz sand	- - - - -	30 per cent.
Litharge	- - - - -	60 „
Saltpetre	- - - - -	10 „
Borax	- - - - -	35 „

Flux H:—

This binding material is frequently styled silver flux. In the process of preparation all the ingredients are intimately mixed with care, in the dry state, and then exposed to the fire in a carefully closed crucible, so that fusion is rapidly and completely effected.

Silver chloride	- - - - -	2½ per cent.
Quartz sand	- - - - -	40 „
Borax	- - - - -	140 „
Litharge	- - - - -	20 „

It must be borne in mind that in fusing these substances excessive heat must be avoided or the silver will be precipitated and found as fine white lumps in the basin of water.

Flux I:—

Silica	-	-	-	-	-	8 per cent.
Minium	-	-	-	-	-	16 „
Borax	-	-	-	-	-	6 „

Fused and treated as for flux D.

Flux K:—

Litharge	-	-	-	-	-	9 per cent.
Silica	-	-	-	-	-	1½ „
Borax	-	-	-	-	-	2 „

Treated like flux I.

The following remarks in relation to the preparation of fluxes apply also to the materials thereof. Before fusing, all the ingredients should be pulverised, well mixed together and then fused. That the materials for fluxes, as well as those for the actual pigments, should be of the best possible quality and free from extraneous admixtures, will be apparent, since, otherwise, results injurious to the beauty and durability of the glazing might be expected.

The fluxes are fused in Hessian crucibles, which should generally be glazed,¹ an operation easily performed in the following manner. A kind of crystal glass is prepared from

Pounded white glass powder	-	-	50 per cent.
Silica	-	-	50 „
Pure lime	-	-	6 „
Potassium carbonate	-	-	22 „

which are heated in a strong fire, cooled and mixed with

Litharge	-	-	-	-	20 per cent.
----------	---	---	---	---	--------------

the mixture being again fused at a strong white heat.

The crucible to be glazed is thoroughly rinsed out with water, and the inner surface covered with the powdered mass. When dry, it is carefully inserted in the fire and heated until the glaze sets fast. Many glass painters merely coat the

¹ Glazing the crucibles prevents the adherence of the fused flux and the escape of lead oxide through the walls of the crucible.

crucible with chalk, by making a mixture of chalk and water and covering the crucible with the same.

When employing used crucibles over again great care is necessary, since the whole colour preparation might easily be spoiled, or contaminated to such an extent as to be unusable.

In a few glass and porcelain painting works the fluxes are fused in the crucibles whilst the porcelain is being fired. When the kiln is drawn the crucibles are broken to get at the flux, which is removed by hammering. It is true that in this way the expense of fusing is lessened; nevertheless, the method is bad, the undue prolongation of heating and the action of moist and reducing gases during the operation causing a loss of lead oxide, and thereby making the flux more refractory. Furthermore, the flux combines with the materials of the crucible at the surface of contact and is rendered less fusible by the silica and alumina so absorbed.

CHAPTER V.

THE COLOUR PASTES.

THERE are a great many colours suitable for glass painting which may, with a suitable amount of care, be easily prepared in large quantities at a time. If the preparation of these colours is always effected with accuracy and according to the same rules, then, naturally, they will always display the same degree of colour, and it is thus possible, by the suitable mixture of a determined quantity of such a colour with an accurately weighed proportion of flux, to prepare a thoroughly permanent and easily reproducible shade of colour.

Those oxides, in particular, which yield perfectly pure—not toned—colours are suitable for the preparation of normal colours. Such are: antimony oxide for yellow, ferric oxide for red, cuprous oxide for red, chromic oxide for green, cobalt oxide for blue and manganese oxide for green. Since these oxides remain unaltered, even by repeated fusings, and at very high temperatures, the preparation of normal colours therefrom is an easy matter, which only requires to be based on great accuracy in weighing the perfectly pure ingredients employed.

A soft, readily fusible glass is selected and converted into very fine powder, which is then intimately mixed with the oxide in question. In order to secure the most perfectly regular admixture possible, it is advisable, when working on a small scale, to employ a mortar; on a large scale, the best results are obtained with rotating barrels.

The mixtures are then compressed in a crucible, the bottom of which is perforated by a central aperture, closed by a close-fitting porcelain rod. The crucible, which must rest on a suitably formed support of fire-resisting earthenware, is heated to strong redness in a furnace (Fig. 1), so that the charge is quickly liquefied. As the mass, although previously tightly compressed, does not, when liquid, more than half fill the crucible, a further supply of the powder is introduced by

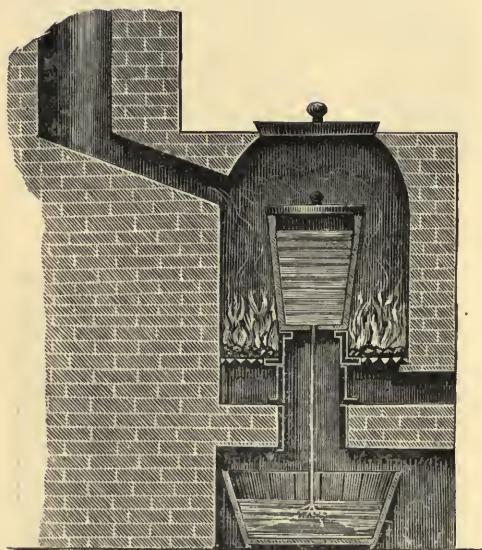


FIG. 1.

means of a ladle until the crucible is quite filled with the molten material, whereupon the porcelain rod is withdrawn.

The fused mass flows through the narrow aperture in the base of the crucible and sets in the water contained in the underlying tub, to form an uncommonly brittle and very readily pulverable glass.

As, however, progress with a single crucible is very slow, and, furthermore, requires a large quantity of fuel, it is

highly advisable, especially when it is desired to prepare colour pastes in quantity, to employ a furnace such as is shown in section in Fig. 2 and in ground plan in Fig. 3.

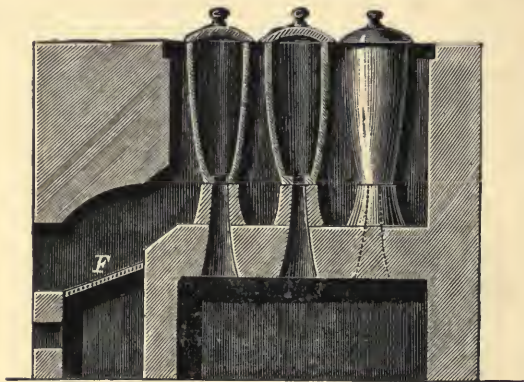


FIG. 2.

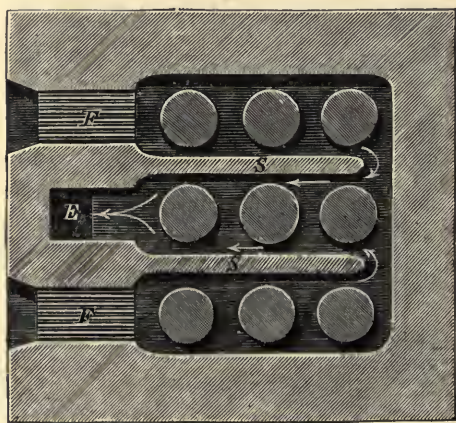


FIG. 3.

As will be seen from the illustrations, this furnace has three compartments, separated by fire-resisting partition walls, S. The flames ascending from both hearths, F, are obliged to take the direction indicated by the arrows in order to

reach the chimney, E, and in their course surround the nine crucibles, which rest on suitable supports and project through the circular apertures, piercing the fireclay plates forming the cover of the furnace, so that the contents of the crucibles can be inspected or fresh powder inserted, without difficulty, by merely removing the lids.

To facilitate simplicity of working, we will select the fol-

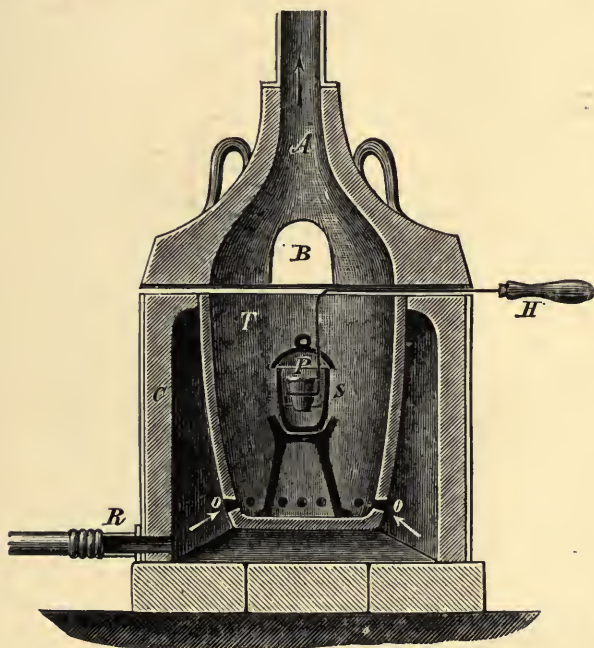


FIG. 4.

lowing proportions of glass, in powder, and the colouring oxides :—

Glass powder	-	-	-	-	-	90 parts.
Colouring oxide	-	-	-	-	-	10 „

The fused charge will then always contain ten per cent. of colouring material. Even this is such a large proportion that glass coloured with cobalt or chrome will not appear

blue or green, but nearly black. In order to now produce, by the help of this dark glass, colours of perfectly accurate shade, we proceed to mix 1, 2, 3, 4, etc., parts of this glass with 99, 98, 97, 96, etc., parts of flux, and fuse the mixture. Small amounts only are taken, *e.g.*, so that the fused mass weighs 100 grams, and in that case the experimental fusing furnace designed by Randau (Fig. 4) can be used.

This furnace consists of a cylinder, C, of fireclay, fitted with a domed cover. In this cylinder stands a large graphite crucible, T, perforated all round the bottom of the side walls by a number of holes, O. A wrought iron tripod, placed in the graphite crucible, supports a smaller fusing crucible, S, into which is lowered by means of the handle, H, a porcelain crucible, P, filled with the mixture of glass and flux. A jet of illuminating gas admitted through the pipe, R, is ignited, and produces such a powerful heat that the contents of the crucible are rapidly fused. As soon as the liquid condition is attained the crucible, P, is removed through the aperture, B, and replaced by another prepared in the interim, so that in this manner, when the apparatus is once heated, a large number of test fusings can be performed in a short time.

Another apparatus also suitable for fusion tests is H. Seger's furnace, shown in Fig. 5.

This consists of a thick-walled fire-brick cylinder, with removable cover, surrounding a high, thin-walled cylinder of fireclay. Inside this fire bridge stands a cylindrical fire-clay capsule (closed by a lid) to hold the substance to be tested. The flame from a six-jet circular Bunsen burner enters the thick-walled, fire-brick jacket through openings bored through the walls for that purpose, ascends around the inner cylinder, and, on reaching the cover, is deflected down-

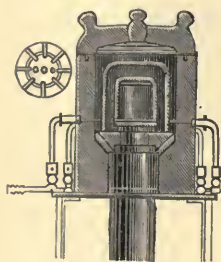


FIG. 5.

wards through the fire bridge and round the capsule into the flue, which communicates with a chimney. The air necessary for combustion is introduced into the annular space, between the jacket and inner cylinder, previously warmed by the flame, and for this purpose the iron flue is surrounded by a jacket; the air rising through the annular space in a direction opposite to that taken by the flue gases, and becoming warmed by contact with the hot surface of the flue pipe. By the direction of the flame, which passes first upwards and then downwards, the actual furnace space is

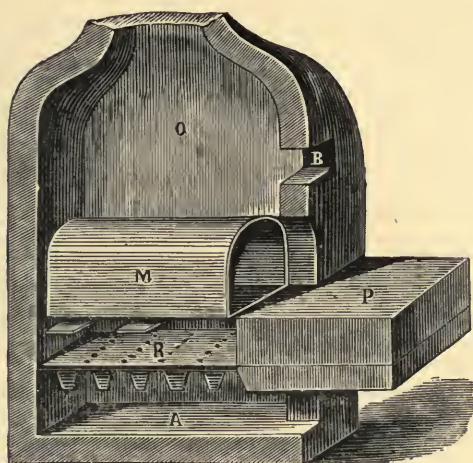


FIG. 6.

surrounded evenly on all sides, and regularity of temperature in all parts of the fusion capsule is thereby ensured. To demonstrate this, the inner space was fitted with a ring of Seger's normal cones and the furnace heated, whereupon the cones subsided regularly. By altering the air inlets in the Bunsen burners one is enabled to employ heating gases of any determined composition. The draught is regulated by a valve in the flue pipe. To set the furnace at work the small inner capsule is charged with the substance to be fused.

Metallic alloys for determining the temperature can also be inserted, and the operation can be overlooked through a hole in the lid of the capsule. A small current of gas is then turned on and carefully ignited. The progress of the fire can be observed through an opening in the cover; the admission of gas is regulated by the supply tap in accordance with the rapidity with which the furnace is to be heated.

The fused fluxes, the colour of which depends on the amount of oxides employed, are powdered and spread in very thin layers on sheets of glass on which the composition of the mass is marked in black flux, *e.g.*, Cr. 5 or Co. 9, meaning that the mass contains in 100 parts 5 parts of glass coloured by chromic oxide, or by 9 parts of cobalt oxide, and so forth.

The glass plates are laid side by side on a clay slab and fired in a small muffle furnace, like the one shown in Fig. 6.

In this way a large number of tints (100 if the mixtures differ progressively by one per cent. of colour) may be produced from each colour, and with the assistance of this palette any given shade of colour can be reproduced with certainty in a glass painting by using the composition indicated on the standard plate.

It cannot be denied that the preparation of these standard colours entails a large amount of tedious labour; nevertheless, this is decidedly repaid by the security with which one can work when possessed of them, and the glass painter who has them at disposal can proceed exactly like his brother artist in oil or water colours by selecting from his voluminous palette the precise colour he considers most suitable for the effect in view.

CHAPTER VI.

THE COLOURED GLASSES.

FOR many effects, particularly for window rosettes and so on, coloured glass panes are used, which, when suitably arranged, form mosaic pictures, producing, by transmitted light in particular, very beautiful effects. Such glass is produced either by colouring the whole mass or by “flashing” the surface of a colourless glass with a layer of coloured glass. In former times, when purple red was produced by gold alone, and yellow solely with silver, this latter method was, in particular, frequently adopted in the preparation of those two colours; at present it is generally the custom to colour the whole of the mass.

In this case the colouring is effected when the glass is fused, and the work is, of course, performed in accordance with well-defined regulations in order to ensure constant regularity of colour and depth.

Behaviour of Glass in Presence of Metals and Metallic Oxides.

The manner in which the various metals and metallic oxides exert a pigmentary action has only been determined in recent times. In this connection the works of W. Müller and Ebell afford a suitable guidance, and the axioms formulated by them are still generally applicable. On this account we subjoin them in full:—

1. Glass is endowed with the property of dissolving

various metals—gold, silver, copper and lead—at a white heat.

2. This solution is effected irrespective of whether the metals are used as such or are precipitated within the substance of the glass by reducing agents. In the latter event the solution is easier and more complete by reason of the finer state of division attainable.

3. The solution of the metals in the glass at white heat is colourless.

4. It remains colourless when the mass is cooled down rapidly.

5. The colourless, solidified solutions of gold, copper and silver change, when moderately heated—to an almost imperceptible red heat—in such a manner that the metal is transformed into an allotropic modification (still soluble) of remarkably high colouring power. Gold and copper glasses become ruby red and silver a fine yellow. This change of colour is designated “running”. Lead exhibits no such action.

6. At a temperature exceeding this “running” heat the metals separate out in crystalline form. Gold glass becomes liver-coloured; copper glass forms either a blood-red mass, “hæmatinon,” coloured by innumerable small crystals, or else a brownish mass, “Aventurin,” clouded by large crystals, according as the temperature maintained is higher or lower; silver glass contains foggy or cloudy deposits; lead glass is blackened by precipitations of the metal.

7. When the temperature is raised to white heat, the original condition is reproduced, the metals again forming colourless solutions.

8. The degree of solubility of the metals is various. Other circumstances being equal, gold is the least soluble, silver being more and copper the most readily dissolved. Silver dissolves so easily that at a temperature whereat the glass

scarcely exhibits the initial signs of softening, the metal is taken up in such large quantity that the glass is coloured intensely (glaze colouring).

9. The comparative solubility of gold varies for the several kinds of glass. Lime, baryta and strontia glasses dissolve so little gold that only a faint colour can be "run" into them, whereas the metal is much more soluble in lead glass. The former kinds necessitate the employment of a much higher temperature for the operation than the latter.

10. A certain time is necessary for the transition from the soluble to the crystalline condition. If the glass, fused at a white heat, is cooled gradually, with great care, clouded glasses—Aventurin, hæmatinon, liver-coloured gold glass—are obtained. Ruby is never produced under these conditions, its solubility being peculiar and only attainable below the crystallisation temperature. Quickly cooled glass retains the colourless appearance of the glass at white heat, the time occupied in cooling being too short for the transition to occur.

11. The change from the colourless to the red condition in gold glass can be effected by prolonged exposure to the influence of light¹ in the same way as by warmth.

Yellow-Coloured Glass.

Yellows are produced in glass by alkali sulphides, antimony, silver or uranium. So far as antimony is concerned, it may only be used in glass that is free from lead. It produces, particularly when employed in conjunction with a little ferric oxide, very handsome colours of very warm shade.

Silver yellow is prepared with silver chloride; this, however, when fused with the glass, frequently produces a turbid, cloudy coloration, so silver chloride is, therefore,

¹ *Dingler's Polyt. Journ.*, vol. cci., 144.

generally employed as a glaze colour by mixing one part of the silver chloride with ten parts of white clay, making it up to a gruel with water and applying the mixture to the glass, which is then fired in a muffle.

The method proposed below is also to be recommended.

To colour glass yellow or red a solution is prepared—according to the *Rev. Scient.*—from 6 grams of gelatine, 1 gram of silver nitrate and 100 grams of water. This mixture is spread on the surface of glasses and dried in the dark. The glasses are next exposed to the light for some time in order to reduce the silver salt contained in the gelatine, whereby a fine pale yellow coloration is developed. With 2 grams of silver nitrate the colour is dark yellow, with 4 grams dark red and red brown. Glass covered with the 7-gram solution of nitrate and dried for eight days in the dark, then carefully washed and redried in the dark, and finally exposed to light, does not show the slightest coloration. If the glass covered with a 4-gram solution be exposed to the action of light in the moist state, the reduction is so complete that the gelatinised surface has quite the appearance of an incomplete metallic mirror. Experiments described by “J. R.,” in the *Sprechsaal* (1889, p. 578), demonstrated, however, that the composition of the glass exerts great influence on the resulting coloration.

Uranium imparts a yellowish-green (canary green) colour, prepared by simply adding uranium oxide to the glass mass. By using

White glass	-	-	-	-	-	200 parts
Uranium oxide	-	-	-	-	-	1 „

a beautiful full yellow-coloured glass is obtained.

Brown-Coloured Glass

can be prepared in all grades of colour by ferric oxide and manganese oxide. It is particularly advisable to employ for

this purpose suitable quantities of the colour pastes already described.

Blue-Coloured Glass

is obtained by means of cobalt oxide and cupric oxide. Both oxides can be fused with the glass direct. Blue sheet glass can be produced by employing from 1 to $1\frac{1}{2}$ parts of cobalt oxide (according to the depth of colour desired) to 1000 parts of sand in the mass. For flash glass, the proportion of cobalt oxide per 1000 parts of sand may be increased to 60 parts. For colouring blue by the aid of cupric acid, 10 to 15 parts of the oxide are taken to every 1000 parts of sand. The addition of an oxidising agent, *e.g.*, saltpetre, to the glass mass is necessary to produce the blue coloration, otherwise if the mass became reduced, the colour would be red (from cuprous oxide) instead of blue.

Green-Coloured Glass.

Greens are produced by the aid of uranium oxide, or by mixtures of ferric and cobalt oxides, or cupric oxide (yellow and blue produce green), and direct by chromic oxide. The cupric-ferric oxide green requires care to prevent the reduction of the cupric oxide to the protoxide condition, which would result in the production of an orange colour (red and yellow forming orange) instead of green.

The following formulæ¹ are recommended for making green glass :—

Light Green :—

Sand	-	-	-	-	-	-	-	100	parts
Potash	-	-	-	-	-	-	-	36	"
Lime	-	-	-	-	-	-	-	14	"
Saltpetre	-	-	-	-	-	-	-	1	"
Uranium oxide	-	-	-	-	-	-	-	1.50	"
Arsenic	-	-	-	-	-	-	-	0.12	"

¹ *Dingler's Polyt. Journ.*, vol. cclxxi., p. 424.

Pompadour Green:—

Sand	-	-	-	-	-	-	-	100	parts
Potash	-	-	-	-	-	-	-	36	"
Lime	-	-	-	-	-	-	-	13	"
Uranium oxide	-	-	-	-	-	-	-	0.75	"
Cupric oxide, black	-	-	-	-	-	-	-	0.38	"
Ferric oxide, red	-	-	-	-	-	-	-	0.75	"
Manganese oxide	-	-	-	-	-	-	-	0.20	"
Arsenic	-	-	-	-	-	-	-	0.12	"

A beautiful green may be imparted to glass by chromic oxide. The solvent power of glass for this oxide is, however, limited, and when an excess of the latter is used it recrystallises out in the form of tiny hexagonal plates in the glass, a green Aventurin glass being the result.

Chrome Aventurin.

According to Pelouze, if

Sand	-	-	-	-	-	-	-	250	parts
Soda	-	-	-	-	-	-	-	100	"
Calcium carbonate (chalk)	-	-	-	-	-	-	-	150	"
Calcium bichromate	-	-	-	-	-	-	-	40	"

be fused together, the above-named separation of chromic oxide takes place, and an Aventurin glass, coloured a deep green by the dissolved oxide, is obtained.

Red-Coloured Glass.

Two bodies producing red colours in glass are known—gold and cuprous oxide. Concerning gold-ruby glass, it should be mentioned that glass can only dissolve at most one ten-thousandth part of its own weight of gold; if more gold be taken it will be found deposited in the metallic state on the bottom of the vessel employed for fusing the mass. Glass which is to be fused with a gold compound must be heated to the strongest white heat, otherwise no purple will be produced, but only a liver-brown glass. One part of gold is capable of colouring 50,000 parts of glass ruby red or 100,000.

parts rose red, provided the materials employed for making the glass are pure.

Gold-Ruby Glass (according to Fuss).

The method recommended by Fuss¹ consists in first preparing a special stock glass, which is then fused, along with the other ingredients, to form the actual ruby glass.

The stock is prepared from :—

Pure quartz	-	-	-	-	-	5 parts
„ minium	-	-	-	-	-	8 „
„ saltpetre	-	-	-	-	-	1 „
„ potash	-	-	-	-	-	1 „

These substances are fused together, poured into water whilst still fluid, and the resulting lead alkali glass finely pulverised.

To prepare the ruby glass,

Stock	-	-	-	40 kilograms
Crystallised borax	-	7.5	„	
Tin oxide	-	0.25	„	
Antimony oxide	-	0.25	„	
Gold (1 ducat)	-	3.4905 grams	(in solution)	

are mixed and fused for twelve hours at not too high a temperature; then left to cool down in the furnace, and the topaz-yellow mass in the crucible is broken up. This, on being warmed, quickly turns to a ruby red. The glass prepared by the above process is particularly adapted for moulding, but less suitable for blowing on account of its great fluidity. A ruby glass for working with the pipe is prepared in the following manner :—

1. *Enamel* :—

Sand	-	-	-	-	-	10 parts
Minium	-	-	-	-	-	8 „
Potash	-	-	-	-	-	1 „
Saltpetre	-	-	-	-	-	1.25 „

¹ *Dingier's Polyt. Journ.*, vol. lx., p. 284.

2. *Glass* :—

Enamel	-	-	-	-	-	35 kilograms
Tin oxide	-	-	-	-	-	0.30 ,,
Antimony oxide	-	-	-	-	-	0.39 ,,
Solution of 1 ducat (see page 163).						

Copper-Ruby Glass.

According to some authorities, metallic copper is the colouring principle in this glass, but others attribute it to dissolved cuprous oxide. The glass should contain neither more nor less than two per cent. of copper, since, when less copper is present, the colour is liable to become blue, and a larger amount renders the glass opaque, transforming it into the opaque blood-red, so-called hæmatinon, glass. On account of its deep red colour copper-ruby glass—which also requires warming for the development of the colour—is most frequently used for flashing. It is of importance, in the preparation of this glass, to prevent oxidation, *i.e.*, the formation of cupric oxide, since this leads to the formation of a blue colour instead of red.

According to Ch. Guignet and L. Magne,¹ red glass does not contain metallic copper—as asserted by Ebell—but cuprous oxide. Accordingly, basic copper chloride, when heated between two plates of glass, gives a red glass immediately by decomposition into cuprous oxide and sodium chloride by the action of the sodium contained in the glass.

Even admitting that cuprous oxide dissolves as metallic copper in the glass under great heat, and produces a red coloration, the process cited is completely affected as soon as the glass softens before the lamp, if at the same time the access of air be prevented. By taking Henrivaux's two formulæ —

¹ *Monit. Céram.*, 1890, p. 26.

	I.	II.
Sodium carbonate - - - - -	100	100
Calcium carbonate - - - - -	50	50
Sand - - - - -	260	260
Cupric oxide - - - - -	10	—
Iron scale - - - - -	—	15

fusing each separately and then mixing them, a dark-green glass, veined with purple, is obtained.

For copper ruby the glass employed may either contain, or be free from, lead.

Lead—free (Flash) Glass :—

Sand - - - - -	100 parts
Soda - - - - -	18 "
Tin oxide - - - - -	20 "
Cupric oxide - - - - -	15 "
Ferric oxide - - - - -	10 "

Lead—Ruby Glass :—

	I.	II.
Sand - - - - -	100	100
Minium - - - - -	166	200
Copper scale - - - - -	7	6
Tin scale - - - - -	7	6

The mass, fused for twelve hours, is quenched and fused over again to render it homogeneous.

According to the specification of Count Schaffgott's Josephine Works (German Patent, No. 76,569), a perfectly transparent massive copper-ruby glass, suitable for direct employment for the manufacture of hollow ware, may be produced by fusing the following charge in an open crucible :—

Fine flint - - - - -	2000 parts
Minium - - - - -	800 "
Potash - - - - -	600 "
Lime - - - - -	100 "
Calcium phosphate - - - - -	20 "
Potassium tartrate - - - - -	20 "
Cuprous oxide - - - - -	9 "
Tin scale - - - - -	13 "

When the mass is fused, hollow glassware of any convenient size and shape may be worked up direct from the crucible.

Violet-Coloured Glass.

This colour can be imparted to the glass by manganese oxide alone, and it is important that the access of any gas exerting a reducing action should be prevented whilst the glass is in a state of fusion, otherwise only a very pale violet glass will be produced. The manganese oxide must also be perfectly free from iron, since the presence of this metal will give the violet a very impure appearance.

Black Glass

is prepared by fusing with any glass a sufficient quantity of powdered chrome ironstone or basalt to colour the glass so strongly that—even when made into thin sheets—it completely absorbs the light, and, therefore, appears black.

CHAPTER VII.

COMPOSITION OF THE PORCELAIN COLOURS.

THE whole of the colours with which we have already become acquainted in the foregoing chapters are also used in painting on porcelain, partly in the same manner as for glass, partly in other combinations and with other fluxes. In painting on porcelain, stoneware and faience, one point lacking in glass painting comes into consideration, and that is the glaze. Should this latter contain tin or lead, then the reactions of these substances with the colouring materials used in the painting will have to be considered. It is mainly the iron colours and gold purple that suffer alteration in presence of such glazes, so that the production of predetermined shades of colour can only be effected with difficulty.

In porcelain painting distinction is also made between various kinds of colours, chiefly :—

1. Such as are not fused ;
2. Such as are fused ; and finally
3. Colours that are fritted.

It is unnecessary to enlarge on the first and second of these classes, since they were thoroughly treated in dealing with glass painting. The third section, which is very important for us in the present instance, includes the most difficult colours, the preparation of which requires great care. These colours are prepared by mixing them with the suitable fluxes and exposing them to the action of fire, whereby the desired shade of colour is developed. The influence of fire

should not, however, be very powerful or sudden, but only sufficient to affect the surface of the colour and to bring the mass to a semi-vitreous state. A fusing heat would be too strong for these colours, and would alter the shade.

We will adopt the combinations of colours for porcelain as prescribed by Brongniart, *viz.* :—

1. Soft muffle colours.
2. Hard muffle colours.
3. Colours for strong fire.

It should be mentioned in this connection that the colours in the first two categories are only used on the glaze itself, whereas those for strong fire are applied below and in the glaze. Of course the colours must in such case be able to withstand the corresponding high temperatures necessary for firing the glazes. It will be apparent that colours of this kind differ considerably from the two first named, which vary but slightly in composition.

Colours are employed on porcelain for :—

(a) Colouring the entire body. These colours are added to and incorporated with the body.

(b) Application to the fused ware (biscuit), which is then coated over with the glaze.

(c) Colouring the glaze, *i.e.*, by mixing the colour with the liquefied glaze and maintaining it in suspension therein during the time the ware is being dipped.

(d) For painting and forming a ground-work on the glaze.

Before examining the various colours in succession, suitable attention will be devoted to the fluxes, of which the assortment employed for porcelain painting is not so varied as for glass. The lead flux, known as Rocaille flux, also plays an important part in this branch. As has been seen, this flux consists of

Litharge, or minium	-	-	-	3 per cent.
Sand	-	-	-	1 „

The more or less decidedly greenish colour of the flux depends on the amount of copper in the litharge or minium; pure and carefully made Rocaille flux should be of a transparent yellowish tinge.

The so-called *grey flux* is employed in two combinations. According to Salvétat :—

Minium	-	-	-	-	-	60 per cent.
Sand	-	-	-	-	-	15 „
Crystallised boracic acid	-	-	-	-	-	25 „
						100

This flux is also used for red and yellow colours. Brongniart prepared *grey flux* by fusing

Minium	-	-	-	-	-	66½ per cent.
Sand	-	-	-	-	-	22½ „
Borax glass	-	-	-	-	-	11½ „
						100

or from

Rocaille flux	-	-	-	-	-	88⅔ per cent.
Borax glass	-	-	-	-	-	11⅓ „
						100

The constituents are mixed, poured out in a fused condition, well pulverised and finely ground.

The *flux for violet* is prepared from

Minium	-	-	-	-	-	67½ per cent.
Sand	-	-	-	-	-	5 „
Crystallised boracic acid	-	-	-	-	-	27½ „

Treated as in the case of grey flux.

Green flux is used for greens, and is prepared by two methods.

Salvétat employs

Minium	-	-	-	-	-	73 per cent.
Sand	-	-	-	-	-	9 „
Crystallised boracic acid	-	-	-	-	-	18 „
						100

Kützen of Meissen makes green flux for the same purpose from

Minium - - - - -	73 per cent.
Sand - - - - -	18 „
Crystallised boracic acid - - -	9 „

Purple flux consists of

Minium - - - - -	37½ per cent.
Sand - - - - -	12½ „
Crystallised boracic acid - - -	50 „

whilst *carmine flux* is made from

Minium - - - - -	11¼ per cent.
Sand - - - - -	33¼ „
Borax glass - - - - -	55½ „

The method of preparation is in all cases similar to that of grey flux. Finally, mention should be made of the *metal flux* prepared with bismuth nitrate. Other varieties of fluxes, beyond those named above, are but seldom used, and, when requisite, will be described in their proper place.

1. SOFT MUFFLE COLOURS.

The muffle colours, whether soft or hard, differ from those for strong fire, in being fired at a much lower temperature than the latter. The muffle colours for enamelled faience are known as reverberatory colours.

The difference between soft and hard muffle colours also consists in the difference of the firing temperatures. By hard muffle colours are understood colours that are vitrified in the muffle, but at a higher temperature than the ordinary (and more usual) soft muffle colours. On this account they are also called “colours for semi-strong fire”.

Reds.—The red colours for porcelain are prepared from almost the same substances as those for glass painting, gold purple and ferric oxide being the most used. We have already

learned how many different shades of red can be obtained by the suitable manipulation of ferric oxide.

A very simple red can be produced from

Ferric oxide (for red)	-	-	-	-	$2\frac{1}{3}$	per cent.
Grey flux ¹	-	-	-	-	$7\frac{2}{3}$	„

simply pounded together. If it is desired to have a somewhat harder colour it is merely necessary to change the ratio of ferric oxide and flux to 1 : 3. These two colours must not be spread out too thickly, or the large proportion of lead glass present will greatly affect the ferric oxide, the colouring power of which will be destroyed.

A fine chamois colour may be easily prepared from

Hydrated ferric oxide ²	-	-	-	-	1	per cent.
Grey flux	-	-	-	-	4	„

These ingredients also merely require to be ground together, and must be laid on thin in painting; the shades obtained are especially suitable for the production of yellow-brown grounds.

The French chemist Salvétat devoted his entire attention to the ferric oxide colours, and the publication of his researches, of so great importance to the porcelain painter, will no doubt be appreciated.

In the first place it is necessary to state that none of the red colours from ferric oxide can be exposed to excessively high temperatures without their colour being injured or totally destroyed; a pale cherry red heat, *i.e.*, 1000° C., should never be attained, and this applies equally to the hard muffle colours. The more—in the preparation of the ferric oxide—the ferrous sulphate is calcined the more will the resulting shades of colour become bluish red. Nevertheless,

¹ Prepared according to Brongniart's recipe, unless stated otherwise.

² Prepared by precipitating ferric oxide solution with liquid ammonia.

the addition of a suitable amount of manganese oxide will produce decided violet and bluish-red tints in a more reliable manner, whilst for yellowish-red shades an addition of zinc oxide (or alum) to the ferric oxide is recommended. The colours concerned will be rendered more lasting and brighter by the admixtures mentioned.

Supported by the experience that the red colours prepared from ferric oxide will vary between yellowish and bluish, according to the mode of calcination, *i.e.*, the lower the calcining temperature the yellower, and the higher the bluer, the shade of colour, it is possible, by accurate methods of working, to make iron preparations which, on being mixed and ground with fluxes, will produce a complete scale of all the red colours. To this end, Salvétat's grey flux is employed, in the proportion of ten per cent. of ferric oxide and forty per cent. of grey flux.

The following recipe is recommended by Brongniart for the preparation of red ferric oxide colours (the author has, however, obtained only unsatisfactory results from its employment) :—

Iron filings	-	-	-	-	-	25 per cent.
Antimony	-	-	-	-	-	25 „
Saltpetre	-	-	-	-	-	50 „

These constituents—the antimony in the metallic state—are well mixed and introduced in successive small quantities into a red hot crucible, where they detonate; the residue is washed, pounded and ground with grey flux in the proportion 1 : 8.

A series of peculiar yellow reds can be prepared as follows: Moistened ferric sulphate is stirred by an iron spatula in a basin placed in an open muffle and calcined, until the greater part of the sulphuric acid is driven off and a sample, when applied in water to the surface of a glass plate, exhibits a fine yellow-red coloration. When cooled, the ferric oxide

is freed from the undecomposed sulphate by washing and is then dried. For the preparation of the actual pigment

Ferric oxide, prepared as above	-	7 per cent.
Grey flux	- - - - -	24 „

are well mixed together and finely ground on a glass plate.

To produce a brilliant brown red the same method is pursued as for yellow red, except that the calcining of the ferric sulphate is prolonged until a sample exhibits a dark-red coloration; the operation is completed in precisely the same way as for yellow red. Isabella and flesh-colour shades may also be very well prepared from ferric oxide, partly from the oxide alone, properly calcined, and partly by mixing ferric oxide and yellow, for which purpose the dark yellow No. 2, that will be described further on, is particularly suitable. The following composition can then be employed :—

Red ferric oxide	- - - - -	1 per cent.
Dark yellow No. 2	- - - - -	4 „
Grey flux	- - - - -	10 „

Simply mixed together and ground down fine on a glass plate.

This colour also can only be worked in thin layers; by admixture with iron red, light blue or dark blue, it can be shaded to taste. The red for cheeks and lips is painted with pompadour red.

When the colours—after firing on the porcelain—are examined under the microscope, they show clearly that the ferric oxide is suspended unchanged in the clear lead glass, the amount that may have been dissolved by the molten lead glass being at any rate so minute as not to have imparted any appreciable coloration.¹

We now come to the production of pompadour red. If ferric sulphate be calcined still more strongly than for brown

¹ According to the valuable researches of Dr. Wächter.

red, it loses its loose structure, becomes heavier and assumes a bluish-red colour. The accurate determination of the moment when the ferric oxide has attained the desired carmine-red shade is not an easy matter, since at this temperature it changes very quickly. The pigment is prepared by mixing

Purple ferric oxide	-	-	-	-	2 per cent.
Subjoined flux	-	-	-	-	5 „

and grinding them down finely on a glass plate.

The flux consists of

Minium	-	-	-	-	-	5 per cent.
Quartz sand	-	-	-	-	-	2 „
Calcined borax	-	-	-	-	-	1 „

the constituents being well fused and treated as usual.

The other red colours, prepared from gold purple, still remain to be described. The rose colours here come first under consideration; the others will be exhaustively described with the violets.

To produce a beautiful rose colour 1 gram of gold is dissolved in aqua regia, the solution mixed with another solution containing 50 grams of alum in 20 litres of spring water, and $1\frac{1}{2}$ grams of a solution of stannous chloride (sp. gr., 1.700) stirred in, followed by ammonia, until all the alumina is thrown down. After the precipitate has subsided the supernatant liquid is poured off and replaced with a similar quantity of fresh spring water, the operation being repeated some ten times running. The residue is then collected on a filter and dried by moderate warmth.

The weight will amount to about $13\frac{1}{2}$ grams, which are then mixed with $2\frac{1}{2}$ grams of silver carbonate and 70 grams of the subjoined flux, and ground fine on a glass plate.

The flux is prepared in the usual manner by fusing

Minium	-	-	-	-	-	2 per cent.
Quartz sand	-	-	-	-	-	1 „
Calcined borax	-	-	-	-	-	1 „

These colours are suitable for the production of pale rose grounds on porcelain, and must be applied as a very thin coating, as, if laid on thick, the gold separates out in the metallic state and the colour disappears. No rose tints prepared from gold are to be found in the old porcelain colours, dating from the last century; one—amaranth red—closely resembling rose, was prepared from light purple. At that time the peculiar property possessed by silver of converting amaranth red into rose red was also unknown, and it was only in the early years of the present (19th) century that the production of rose-red colours on porcelain was effected at the Royal Porcelain Works, Berlin, then under the management of Dr. Richter.

Blue colours are prepared solely with cobalt oxide. The employment of only the purest and most carefully prepared oxide is assumed.

Pale blue tints are produced with

Cobalt oxide	-	-	-	-	-	1 per cent.
Zinc oxide	-	-	-	-	-	2 „
Rocaille flux	-	-	-	-	-	6 „
Salvétat's grey flux	-	-	-	-	-	1½ „

These substances are well mixed and fused in a porcelain crucible for at least three hours at red heat, then poured out, broken up and ground fine on a glass plate. To produce a fine tone, prolonged fusion at not too high a temperature is essential.

A beautiful *sky blue*, chiefly adapted for painting the skies in landscapes, is prepared by the intimate mixture and fine grinding (on a glass plate) of

Dark blue (see below)	-	-	-	-	-	2 per cent.
Zinc oxide	-	-	-	-	-	1 „
Rocaille flux	-	-	-	-	-	4 „

The colour may be either used alone or in conjunction with others.

A brilliant blue, mainly suitable for shading, may be obtained from

Cobalt oxide	-	-	-	-	-	10 per cent.
Zinc oxide	-	-	-	-	-	9 „
Salvétat's grey flux	-	-	-	-	-	5 „
Rocaille flux	-	-	-	-	-	25 „

treated as for pale blue. This colour is only used for shading, either under or over the blues described above, for which purpose its refractory nature renders it particularly suitable.

All these blue pigments, after they have been fired on the porcelain, exhibit under the microscope a mixture of a transparent blue substance¹ with a colourless glass, instead of consisting of a homogeneous blue glass.

The following recipe is typical for dark blue colours :—

Cobalt oxide	-	-	-	-	-	1 per cent.
Zinc oxide	-	-	-	-	-	1 „
Salvétat's grey flux	-	-	-	-	-	1 „
Rocaille flux	-	-	-	-	-	4 „

These are well mixed and treated like the pale blue colours. When allowed to cool slowly the colour consists of an agglomeration of pointed crystals. The most essential condition for the successful production of a fine dark blue is prolonged fusion at not too high a temperature.

According to a French recipe, a dark blue is produced by

Cobalt oxide	-	-	-	-	-	13 per cent.
Zinc oxide	-	-	-	-	-	20 „
Grey flux	-	-	-	-	-	61 „

Well mixed and then fused. The resulting colours are miscible with violet and red gold preparations only, all other colours changing the blue into grey or black.

A blue much sought after is *turquoise blue*, a very accurate recipe (Dr. Wächter's) for which is appended. This is all the more worthy of recommendation because the recipe for

¹ Cobalt-zinc silicate ?

turquoise blue given in Brongniart's work is decidedly erroneous, in that the flux used by him for this colour (consisting of minium 60 per cent., pure crystallised boracic acid 20 per cent., and sand 20 per cent.) completely destroys the turquoise blue colouring matters when fused, and only yields a dirty blue-green colour as the result. Strele—at one time manager of the former Royal Porcelain Works at Vienna—confidently reproduced this and other similar errors of Brongniart.

The communications published both in trade journals and large works on the manufacture of porcelain colours are all tarred with the same brush, being—although we have no desire to pronounce a general dogmatic condemnation—all and sundry too incomplete and unreliable to afford accurate guidance. Even in the renowned work of Brongniart,¹ which contains much that is really novel and valuable, the chapter on the preparation of colours is of a very unsatisfactory character. The author, although having voluminous material at his disposal, cites old recipes from glass painters and newer ones from French manufacturers, but in no case gives without reserve particulars of the experience gained in the Royal Porcelain Works at Sèvres; and a few of the recipes are altogether incorrect. The same must be recorded of the above-named Strele. Take it as one will, the preparation of fine and good pigments is still, as it was a hundred years ago, maintained as a profound secret. A modern chemist, specially engaged in this class of work, correctly observes in this connection that, so long as any one desirous of taking up the matter is obliged to begin at the beginning and obtain for himself the experience already acquired, but kept secret, by others, before he can attain even to the present new standpoint of the empiricist, so long will the prospect of having to devote such an amount of time and trouble

¹ *Traité des Arts Ceramiques.*

to this end frighten away the majority, to the great disadvantage of the progress of the art. This is especially true as regards scientific chemists, to whom so many other promising fields of investigation are open.

Turquoise Blue:—

Cobalt oxide	-	-	-	-	-	3 per cent.
Pure zinc oxide	-	-	-	-	-	1 „

are dissolved together in pure sulphuric acid. To the solution is added a 40 per cent. solution of ammonium alum, the mixture being thereupon evaporated to dryness and the residue heated until all the water is driven off. It is then powdered and exposed to a brisk red heat for several hours in a crucible.

The colour comes out best when it has been exposed to the heat of the furnace during the firing of a batch of ware. It consists of a compound of about 4 equivalents of alumina, 3 equivalents of cobalt oxide and 1 equivalent of zinc oxide, and exhibits a fine turquoise blue colour; if the above proportions of the oxides be varied, the colour will not be so fine. A greenish tinge may be imparted to turquoise blue, when desired, by the introduction of freshly precipitated, moist mercurous chromate into the solution of ammonia, alum, zinc and cobalt; $\frac{1}{16}$ part of mercurous chromate (calculated in the dry state) will suffice for the quantities given above.

The turquoise blue paste is prepared by mixing together

Aluminium-cobalt-zinc oxide (as above)	-	-	1 per cent.
Metal flux	-	-	2 „

The metal flux is prepared for this purpose by fusing together

Bismuth oxide	-	-	-	-	5 per cent.
Crystallised boracic acid	-	-	-	-	1 „

Microscopic examination of the turquoise blue colour when fired on the porcelain shows it to consist of a mixture of a transparent blue substance and a colourless glass. The

transparent blue substance is in all probability the aluminium-cobalt oxide described, which is, by itself, transparent under the microscope; this property being, however, considerably increased by the surrounding fused bismuth oxide, in the same manner as paper fibres are rendered transparent by oil. The same applies also to the microscopic blue constituents of the other blue pastes, which are probably cobalt-zinc carbonate, this substance forming, by itself, when examined microscopically, a pure transparent blue powder.

The *yellow* colours for porcelain painting consist of glasses prepared either from antimoniac acid or uranium oxide. The potassium antimoniate necessary thereto is prepared by detonating one part of finely ground metallic antimony with two parts of saltpetre in a red hot Hessian crucible, and well washing the residue with water. The uranium oxide is obtained in the most suitable form by heating uranium nitrate until the nitric acid is completely driven off. This subject will be found exhaustively discussed in chapter ii., under antimony oxide and uranium oxide.

For orange, lead chromate is occasionally used.

Pale yellow shades may be readily prepared in the following manner:—

Potassium antimoniate	-	-	-	4 per cent.
Zinc oxide	-	-	-	1 „
Lead glass	-	-	-	36 „

Well mixed together, fused in a Hessian crucible, pounded when cold and ground fine.

The lead glass is made by fusing

White sand	-	-	-	1 per cent.
Minium	-	-	-	8 „

Prolonged fusion is not injurious in the preparation of this fine yellow, no boracic acid being present. The colour is very powerful, and is, therefore, well adapted for mixing with red or blue colours, but less so with green.

A beautiful *citron yellow*—though not such a powerful colour as the one just described—is obtained from

Potassium antimoniate	-	-	-	8 per cent.
Zinc oxide	-	-	-	2½ „
Brongniart's grey flux	-	-	-	36 „

The ingredients are thoroughly well mixed and then calcined in a porcelain crucible (standing in a Hessian crucible) until the contents have fused to a gruelly liquid; whereupon they are removed by the spatula, pounded when cold, and finely ground on a glass plate. If the colour be fused longer than is absolutely necessary for perfect intermixture of the constituents, the yellow colour is changed into a dirty grey, owing to the destruction of the lead antimoniate. This yellow does not mix well with red and brown, but, on the other hand, produces very pure shades of colour along with green.

The above-named pale yellow is in many respects preferable to this citron yellow, being, on account of its greater density, more ready to leave the brush, and may, moreover, be applied in thicker layers than the citron yellow without tending to spring off when fired. Less care is also required in fusing the pale yellow than in treating the citron.

Dark yellow may be prepared from potassium antimoniate in two ways, *viz.*, with or without borax.

A fine *golden yellow* is obtained by fusing

Potassium antimoniate	-	-	-	16 per cent.
Zinc oxide	-	-	-	4 „
Ferric oxide	-	-	-	5 „
Litharge	-	-	-	48 „
Quartz sand	-	-	-	16 „
Calcined borax	-	-	-	18 „

In this case also the presence of borax renders the prolongation of fusing beyond the time necessary for the complete union of the various constituents decidedly injurious, for the same reason as mentioned for citron yellow, the golden-yellow colour being then easily transformed into a

dirty yellow brown. Another dark yellow, without borax, can be obtained by fusing

Potassium antimoniate	-	-	-	-	4½ per cent.
Ferric oxide	-	-	-	-	1 „
Zinc oxide	-	-	-	-	1 „
Minium	-	-	-	-	20 „
White sand	-	-	-	-	2½ „

Protracted fusion is here less injurious than for the preceding golden yellow. An iron-red colour may be used for painting upon or beside this yellow, without the colour being destroyed or injuriously tinged.

The yellow paste colours prepared with antimony, when examined microscopically after firing on porcelain, do not appear as homogeneous yellow glass, but as mixtures of a transparent yellow substance (lead antimoniate, according to Wächter) and a colourless glass.

For landscape and figure painting it is important to make the yellow colours somewhat more refractory, so that they may be painted under or over without fear of the colour being dissolved by the colours laying above or underneath. This property is communicated by the addition of Naples yellow, which is most suitably prepared for this purpose by strongly calcining a mixture of

Tartar emetic	-	-	-	-	-	1 part
Lead nitrate	-	-	-	-	-	2 „
Crepitated common salt	-	-	-	-	-	4 „

in a Hessian crucible for a long time, and afterwards washing out the pulverised residue with water. By mixing this Naples yellow with lead glass the same end may be served, but in a less economical manner. For example, a good yellow for landscape painting is yielded by a mixture of

Naples yellow	-	-	-	-	-	8 per cent.
Salvétat's grey flux	-	-	-	-	-	6 „

A fine yellow, unfortunately only suitable for certain purposes, is prepared from uranium oxide,

Uranium oxide -	-	-	-	-	-	2 per cent.
Lead glass	-	-	-	-	-	8 „

being intimately mixed and ground till fine on a glass plate. The lead glass consists of

Minium -	-	-	-	-	-	8 per cent.
Sand -	-	-	-	-	-	1 „

which are fused together. The yellow is totally destroyed if mixed with other colours, but, on the other hand, may be shaded by the employment of dark purple and violet. Exactly the same properties, so far as mixing with other colours is concerned, are exhibited by the orange obtained from uranium oxide, and very frequently used on account of its handsome colour. To prepare this paste:—

Uranium oxide -	-	-	-	-	-	2 per cent.
Silver chloride -	-	-	-	-	-	1 „
Bismuth glass ¹	-	-	-	-	-	3 „

are intimately mixed and finely ground on a glass plate.

Examined under the microscope, the uranium yellow and orange colours fired on porcelain appear as a pale yellow-coloured glass, containing unchanged uranium oxide in suspension; a small portion of uranium oxide is therefore dissolved. According to Bunel, a full dark orange can be obtained with lead chromate, equal parts of minium and lead chromate being taken and fused over a good fire. This orange also is unsuitable for mixing with other colours.

Green colours are, for the most part, prepared with chromic oxide, or with mercury chromate and cobalt; mixtures of blue and yellow are also often employed. The use of cupric oxide, which from the earliest times was known to

¹ Prepared by fusing four parts of bismuth oxide with one part of crystallised boracic acid.

produce green colours (as exemplified in ancient Arabian and Egyptian pottery), has now entirely ceased.

An entire series of very fine and brilliant green colours is prepared by the following method, which is reliable:—

Mercurous chromate	-	-	-	10 per cent.
Chemically pure cobaltic oxide	-		1	„

are ground by means of a muller on a glass plate in order to secure intimate admixture, and then heated in a porcelain tube, open at both ends, until all the mercury is driven off. The fine blue-green powder so obtained is then transferred to a porcelain crucible, the lid of which is luted with glaze. The filled crucible is exposed to the strongest heat of the porcelain kiln during the time a charge of ware is being fired, and after cooling, the crucible is broken up and the contents removed to be washed with water for the extraction of the small quantity of potassium chromate.

In this manner a compound of chromic oxide and cobalt oxide, in almost identical equivalents, is obtained, possessing the blue-green colour of verdigris. The requisite blue-green paste, which is used as an enamel, is then compounded from

Chromic-cobalt oxide (as above)	-		1 per cent.
Zinc oxide	-	-	$\frac{1}{2}$ „
Grey flux	-	-	5 „

well incorporated together and ground fine on a glass plate. By mixing this colour—which by itself forms a fine blue-green—with citron yellow (see above) all the intermediate tints of green can be obtained. So, for example, a very brilliant and bright *grass green*, with

Stock colour	-	-	-	1 per cent.
Citron yellow	-	-	-	6 „

A full *dark green* is obtained when mercurous chromate by itself is subjected to the same treatment as indicated for blue green; the mixture of the same with cobalt oxide and one part of the fine green chromic oxide, so obtained, is

mixed with three parts of grey flux and ground down fine on a glass plate.

To produce a dark green, Brongniart recommends the admixture and fusion of

Chromic oxide	-	-	-	-	7½ per cent.
Cobalt oxide	-	-	-	-	2½ „

2½ per cent. of this mixture being mixed with 7½ per cent. of flux for green, without fusing.

A soft dark green may be obtained by taking 1 part of oxide to 4 parts of flux.

Very often the production of *brown-green* colours is necessary, a colour particularly advantageous for breaking the pure greens in landscape painting. Such a brown green can be obtained by mixing dark green with yellow ochre, wood brown and sepia brown in various proportions, but it is difficult to exactly hit off the desired tone in this manner, and the amount of brown will always have to be exceeded. A better material for attaining this object is the off-coloured (brown) oxide, produced in the preparation of chromic oxide. It is only necessary to mix this brownish oxide with the green flux in the proportion of 1 : 3.

A good shading green is obtained by carefully mixing

Mercurous chromate	-	-	-	-	8 per cent.
Pure cobalt oxide	-	-	-	-	1 „

and heating the mixture on a flat dish in the strongest heat of the porcelain kiln whilst a charge is being fired. A greenish-black chromic-cobalt oxide is produced, which, when mixed with twice its weight of grey flux, yields a refractory black-green colour for shading other greens.

If thin splinters of the chrome green colours fired on porcelain be examined under the microscope, the particles of chromic oxide or chromic-cobalt oxide will be seen imbedded undissolved in the colourless lead glass.

In certain cases chromic oxide cannot be used for greens

for porcelain, especially when the mass fuses at the heat necessary for firing. In such instances greens prepared from copper must be employed, for which a few recipes from the Sèvres Works are now appended :—

No. 1 :—

Minium	-	-	-	-	-	34 per cent.
Ferric oxide (precipitated by ammonia)	-	-	-	-	-	33 „
Dark yellow ¹	-	-	-	-	-	33 „
						100

Fused together.

No. 2 :—

Opal yellow-green enamel	-	-	67 per cent.
Minium - - - -	-	-	33 „
			100

Fused together.

By mixing these two in equal parts the stock for the following colours is obtained :—

Emerald Green :—

Stock	-	-	-	-	-	92 per cent.
Dark blue	-	-	-	-	-	8 „
						100

Grind and fuse.

Emperor Green :—

Stock	-	-	-	-	-	86 per cent.
Dark blue (as above)	-	-	-	-	-	14 „
						100

Proceed as for emerald green.

Dark Green :—

Stock	-	-	-	-	-	75 per cent.
Dark blue	-	-	-	-	-	25 „
						100

Prepared in the same manner.

¹ This dark yellow is prepared by fusing

Naples yellow	-	-	-	-	32 per cent.
Red ferric oxide	-	-	-	-	4 „
Rocaille flux	-	-	-	-	60 „

We come now to the *violet* colours, which are, for the most part, produced from gold purple. For certain violet foundations manganese oxide is also occasionally used. The colouring materials in the violets prepared from gold purple are gold preparations, the production of which necessitates the greatest attention and care. The preparation of the gold purple will be given in all the various cases now in question.

Light purple colours are obtained in the following manner: Five grams of tin turnings are dissolved in boiling aqua regia and the solution concentrated in the water bath until it sets on cooling. The chloride of tin so prepared, and which always contains an excess of hydrochloric acid, is dissolved in a very small quantity of distilled water and mixed with two grams of a solution (sp. gr., 1·700) of protochloride of tin (stannous chloride), obtained by boiling tin turnings in an excess of hydrochloric acid until sufficiently concentrated.

The mixed tin solution is poured into a glass vessel and gradually mixed with ten litres of distilled water. It must still contain sufficient acid to prevent coloration from the deposition of tin oxide; for this a preliminary test must be made by dropping a little of the solution from a glass rod into distilled water. To this diluted tin solution is now added, with constant stirring, a clear solution (as nearly neutral as possible) of 0·5 gram of gold in aqua regia; this must have previously been evaporated almost to dryness in the water bath, then diluted with water and filtered in a dark place. On the addition of the gold solution the entire liquid assumes a deep red coloration, without, however, any precipitate being formed, but this will come down at once on the addition of 50 grams of liquid ammonia. If, as may happen when the proportion of ammonia is too great as compared with the acid in the solution (in which case the liquid forms a deep red solution), this does not occur, it will

do so immediately on the addition of a few drops of concentrated sulphuric acid. The precipitate very quickly subsides and the supernatant liquid must be poured off as soon as possible and replaced by an equal quantity of fresh spring water, an operation repeated five or six times in succession. After the precipitate has thus been thoroughly washed, it is collected on a filter and well drained, whereupon, whilst still moist, it is carefully removed by a silver spatula on to a ground glass plate and intimately mixed by a spatula and muller with 20 grams of lead glass, previously ground down fine in water. This glass is prepared from

Minium	-	-	-	-	-	2 per cent.
Quartz sand	-	-	-	-	-	1 „
Calcined borax	-	-	-	-	-	1 „

The mixture of gold purple and lead glass is slowly dried on the same glass plate, in a moderately warm room and in a situation where dust can be carefully excluded, and is then ground along with 3 grams of silver carbonate. The resulting purple from the original 0.5 gram of gold amounts to about 35 grams.

This proportion of lead glass and silver carbonate is only suitable for gold precipitate for a certain degree of firing heat, which approximates very closely to the fusing point of silver (*i.e.*, not quite 1000° C.). For firing at a lower temperature the ratio of lead glass to gold must be increased, but that of the silver chloride lessened. The best of purple colours may be ruined in firing; if fired at too low a temperature the colour remains brown and dull, and if the suitable temperature be exceeded, the colour then appears bluish and faint. Reducing gases, and especially acid vapours, as well as the vapours of bismuth oxide, etc., also have an injurious effect.

Darker purple is prepared in a similar manner to light purple; the clear and (as nearly as possible) neutral solution of 0.5 gram of gold in aqua regia is diluted with 10 litres of

water in a glass vessel, and 7·5 grams of the above described stannous chloride solution (sp. gr., 1·700) carefully stirred in. The liquid is coloured a deep brown red, but the precipitate only comes down after a few drops of concentrated sulphuric acid have been added. The supernatant liquid is poured off and the precipitate washed by the addition of an equal quantity of water, five or six times repeated. The thoroughly washed precipitate is well drained on a filter, removed in a still moist condition by a spatula, and treated in the same manner as for light purple, by mixing with 10 grams of the aforesaid lead glass, dried and mixed dry with 0·5 gram of silver carbonate, and ground fine; in this way some 13 grams of dark purple are obtained.

The proportions of lead glass and silver carbonate to gold precipitate apply for the same firing heat as mentioned in connection with light purple; for lower temperatures the ratio of lead glass to gold must be increased, and that of silver diminished. Both these colours are very suitable for mixing with dark blue, but less so with the yellow-brown colours prepared from ochre.

To produce a brilliant *red violet* shade, the gold precipitate from 0·5 gram of gold is prepared as described for dark purple, and is then, after removal in the moist state from the filter, mixed with 12 grams of a flux obtained by fusing together

Minium	-	-	-	-	-	4 per cent.
Quartz sand	-	-	-	-	-	2 „
Calcined borax	-	-	-	-	-	1 „

The mixture of flux and gold precipitate is dried and ground on the glass plate once more, but without any addition of silver. Here again the ratio given between lead glass and gold is only suitable for the firing temperature named for the pale and dark purple, a lower muffle temperature necessitating an increase of the flux. Lowering the propor-

tion of silver in this colour converts the red violet into dark purple, and if employed for glass painting it produces by itself a fine purple tone.

In order to produce a *blue violet*, it is merely necessary to intimately mix the same precipitate as for red violet, from 0.5 gram of gold, in a moist state on a glass plate along with 10.5 grams of a flux prepared by fusing together

Minium	-	-	-	-	-	4 per cent.
Quartz sand	-	-	-	-	-	1 „

afterwards slowly drying the same, as for the other colours, and grinding again on the glass plate. A lower muffle temperature in firing necessitates a higher proportion of flux. This blue violet is specially adapted for mixing with blues, by which it is less injuriously shaded than red violet. It is unsuitable for glass painting. The most important factor in the production of good purples and violets is the fine state of division, first of the gold in the precipitate, and then of the precipitation of the gold in the flux. The latter is facilitated by the mixture of the still moist precipitate with the flux itself.¹

The whole of the gold colours here mentioned, when fused by themselves in the crucible, do not, as one would suppose, produce red or violet coloured glasses, but dirty brown or yellowish glasses, with a cloudy appearance, due to precipitated metallic gold or silver. Their proper fine colour shades are only developed when they are fused on the surface of the porcelain, in layers of not too great a thickness. These they colour through and through, as examination of a section of a broken piece of painted porcelain will reveal.

¹ In the application of the gold colours to biscuit porcelain or faience, the amount of lead in the glaze has also to be considered, since, in association with the lead in the flux, it exercises an injurious influence on the violet colours. In such cases the amount of minium or litharge in the flux must be decreased.

When the layer exceeds a certain thickness the metallic gold and silver separate out, and the layer becomes thereby either cloudy, as in the case of the purples and violets, or even colourless, as in the case of the liquid rose colour.

A good violet can be prepared from manganese oxide, according to the following prescription:—

Sand	-	-	-	-	-	3½ per cent.
Potassium carbonate	-	-	-	-	-	1½ „
Saltpetre	-	-	-	-	-	8½ „
Minium	-	-	-	-	-	4½ „
Borax glass	-	-	-	-	-	½ „
Manganese oxide	-	-	-	-	-	2 „

These are mixed and calcined in a Hessian crucible until the whole mass is fluid; then poured out, left to cool, powdered and finely ground on a glass plate.

This colour is applied in two layers.

The *brown* colours are obtained by means of ferric, zinc and cobalt oxides, manganese oxide being also often used. Light browns are mostly produced from ferric oxide, whilst for dark brown tones an addition of cobalt oxide is made.

Beautiful *light brown* shades—in three different tints—are produced by the following method:—

Calcined ferrous sulphate	-	-	-	-	6 per cent.
Dehydrated zinc sulphate	-	-	-	-	4 „
Saltpetre	-	-	-	-	13 „

Well mixed and heated to redness in a Hessian crucible until the saltpetre is completely decomposed; when cooled the crucible is broken, the residue removed and freed from soluble matter by boiling with water. A grey-brown powder—a compound of zinc oxide and ferric oxide—is left. The paste is prepared by mixing and grinding

Zinco-ferric oxide	-	-	-	-	2 per cent.
Subjoined flux	-	-	-	-	5 „

To prepare the flux:—

Minium	-	-	-	-	-	12 per cent.
Quartz sand	-	-	-	-	-	3 „
Calcined borax	-	-	-	-	-	1 „

are fused together, pounded on cooling and ground fine on a glass plate.

The second light brown shade is produced by treating

Calcined ferric oxide	-	-	-	-	2 per cent.
Dehydrated zinc sulphate	-	-	-	-	2 „
Saltpetre	-	-	-	-	5 „

as described above, the resulting zinco-ferric oxide being mixed in the same proportion with the same flux and finely ground.

The third shade is prepared from

Calcined ferric oxide	-	-	-	-	2 per cent.
Dehydrated zinc sulphate	-	-	-	-	2 „
Saltpetre	-	-	-	-	4 „

treated as detailed for the other two shades.

These colours, when fired on porcelain, exhibit under the microscope transparent particles of yellow zinco-ferric oxide suspended in the colourless lead glass.

A most extensive variety of *chestnut browns*, even as far as black, are obtainable from ferric oxide used by itself, by exposure to a still greater heat than is required for producing the red shades, and mixing

Chestnut brown ferric oxide	-	-	-	-	2 per cent.
Flux for light brown	-	-	-	-	5 „

grinding fine as usual.

A so-called *bistre brown* is prepared in a similar manner to that described for light browns, only that here an addition of manganese oxide is made to the ferric and zinc oxides. The recipes of two shades, a dark and a lighter bistre, are given below :—

Bistre Brown (a):—

Calcined manganese oxide	-	-	1 per cent.
„ ferrous sulphate	-	-	12 „
Dehydrated zinc sulphate	-	-	8 „
Saltpetre - - - -	-	-	26 „

treated as described for the first shade of light brown, the dark brown powder—a combination of zinc oxide, ferric oxide and manganese oxide—thus obtained being mixed and finely ground with $2\frac{1}{2}$ times its weight of the same flux as is used for the other browns.

Bistre Brown (b):—

Calcined manganese oxide	-	-	1 per cent.
„ ferrous sulphate	-	-	4 „
Dehydrated zinc sulphate	-	-	5 „
Saltpetre - - - -	-	-	12 „

treated as for bistre brown (a).

Brown Red:—

A suitable shade of ferric oxide is prepared and mixed with grey flux in the proportion of 1 : 3.

Next to be considered are the *sepia browns*, for which various methods of preparation may be adopted. According to a French recipe given by Bunel, the subjoined procedure may be followed:—

Ferric oxide, precipitated by ammonia	-	11 $\frac{3}{4}$ per cent.
Zinc oxide - - - -	-	11 $\frac{3}{4}$ „
Cobalt oxide - - - -	-	5 $\frac{1}{2}$ „
Brongniart's grey flux - - - -	-	70 „

These constituents are fritted at a moderate heat, and, in place of Brongniart's grey flux, that prepared [according to Salvétat's formula may be employed. This brown can be very easily shaded by substituting for the ferric oxide precipitated by ammonia the yellow ferric oxide thrown down during the spontaneous decomposition of ferrous sulphate solution. The resulting colour mixes well with all others.

Medium Sepia Brown :—

Calcined ferrous sulphate	-	-	-	1 per cent.
„ manganese oxide	-	-	-	1 „
Dehydrated zinc sulphate	-	-	-	2 „
Saltpetre	-	-	-	5 „

Treated as for the first light brown, the resulting yellow-brown pigment being mixed with $2\frac{1}{2}$ times its weight of the same flux and finely ground.

Dark Medium Sepia Brown :—

Calcined ferrous sulphate	-	-	-	1 per cent.
„ manganese oxide	-	-	-	2 „
„ zinc sulphate	-	-	-	6 „
Saltpetre	-	-	-	10 „

are treated in the usual manner, and the paste made up from the resulting colouring matter.

Yellow-brown colours are most easily prepared from ferric oxide, but unfortunately do not vitrify well.

For Nankin yellow :—

Yellow ferric oxide	-	-	-	6 per cent.
Zinc oxide	-	-	-	13 „
Grey flux	-	-	-	80 „

are taken and merely ground down fine together.

Dark ochre yellow is prepared by carefully mixing and grinding

Yellow ferric oxide	-	-	-	$12\frac{1}{2}$ per cent.
Zinc oxide	-	-	-	$12\frac{1}{2}$ „
Grey flux	-	-	-	75 „

Strele proposed to employ aluminium hydrate instead of zinc hydrate, as producing lighter and more durable ochre colours. The aluminium hydrate is prepared by precipitation by an excess of ammonium carbonate solution from a solution of alum, and washing the precipitate with boiling water.

Fine dark-brown colours can be obtained from the following recipe :—

Calcined cobalt sulphate	-	-	1 per cent.
Dehydrated zinc sulphate	-	-	4 „
Ferrous sulphate	-	-	4 „
Saltpetre	-	-	10 „

mixed and treated as for light brown; the fine, dark reddish brown combination of the oxides of cobalt, zinc and (ferric) iron thus prepared, is mixed with $2\frac{1}{2}$ times its weight of the flux for sepia browns and ground fine.

Chrome Brown :—

One per cent. of hydrated ferric oxide is mixed with two per cent. of mercurous chromate and ground on a glass plate to ensure intimacy of admixture, then heated to redness on a plate in the open muffle until all the mercury is driven off. The resulting dark red brown compound of chromic oxide and ferric oxide is mixed with three times its weight of grey flux and finely ground on a glass plate.

When fired on porcelain and examined under the microscope, the various brown colours display the dark coloured oxide compounds in a state of suspension, and not, or at any rate very little, in solution in the lead glass. The dry methods of preparing the oxides forming the colouring materials for the various shades of brown, are cheaper and more reliable than by precipitating the mixed solutions by sodium carbonate and calcining the washed precipitate, which would also produce the same results. If the individual oxides, and not the combination of oxides, are mixed with the lead glass, then the resulting colours will not come out of the ordeal of firing pure, *i.e.*, the colour in thick layers will be of a different tone to that where the layers are thinner; moreover, their colour before firing will differ from the shade finally produced, on which account they are unreliable for the painter's use.

The *grey* colours are obtained by suitable admixtures of the oxides of (ferric) iron, manganese and cobalt, with a

fairly large proportion of flux. Should the temperature to which the greys are exposed in the muffle be too high, the shades will soon be altered thereby, partly by disappearance, partly by turning black, impure and lustreless.

The first two recipes subjoined are French.

Dark Grey (for groundwork), according to Salvétat:—

Yellow ferric oxide	-	-	-	4 per cent.
Cobalt oxide	-	-	-	8 „
Salvétat's grey flux	-	-	-	88 „
				100

Ground well together and fused at a moderate heat.

Dark Grey, according to Bunel:—

Yellow ferric oxide	-	-	-	13 per cent.
Zinc oxide	-	-	-	13 „
Cobalt oxide	-	-	-	6 „
Flux for grey	-	-	-	68 „
				100

Treated as for the first dark grey.

Mouse Grey:—

Calcined cobalt sulphate	-	-	-	2 per cent.
Dehydrated manganese sulphate	-	-	-	2 „
Saltpetre	-	-	-	5 „

Well mixed together and heated to redness in a Hessian crucible until the saltpetre is completely decomposed. The calcined mass leaves, on boiling with water, a deep black powder, a combination of manganese and cobalt oxides. To prepare the grey paste

Mangano-cobaltic oxide	-	-	-	2 per cent.
Zinc oxide	-	-	-	1 „
Grey flux	-	-	-	10 „

are mixed and ground fine. By frequent firing this grey easily changes in shade, and it is, moreover, ill adapted for mixing with other colours.

A fine *bluish grey* can be easily prepared from

Dark grey (Bunel)	-	-	-	5 per cent.
Sky blue	-	-	-	5 „

Light grey shades may be made up as follows:—

Cobalt oxide - - - - -	5 per cent.
Yellow ferric oxide - - - -	3 „
Salvétat's grey flux - - - -	92 „
	100

These ingredients are fused at a moderate heat, or it is sufficient to frit the mass by inserting in a double crucible, so that the heat may penetrate more slowly.

Reddish grey tints are prepared, according to Salvétat, with

Cobalt oxide - - - - -	6 per cent.
Red ferric oxide - - - - -	3 „
Zinc oxide - - - - -	3 „
Salvétat's grey flux - - - -	88 „
	100

These substances are ground up together and heated to a temperature sufficient to frit the mass. In making this grey for grounds, the amount of the flux is increased to 95 per cent. This colour may also be employed for shading on carnation, since it mixes well with all colours and vitrifies satisfactorily.

One of the handsomest, tenderest, and at the same time most durable of the greys is *platinum grey*; unfortunately it is dearer than any other of these colours. One of its chief advantages is its permanence under the strongest red heat, a property the advantage of which, as compared with other greys, will be apparent from the following observations.

As is well known, black is always produced when the oxides of iron and cobalt, or cobalt, iron, manganese or copper are fused in large amount, especially in presence of a fusible siliceous material. The production of the above-mentioned greys, and of the blacks to be described later, is based on this reaction. The shade may be varied by altering the quantitative proportions of the oxides. Strele correctly

remarks in this connection: "When the painter blends a blue, red or ochre yellow by an admixture of ordinary grey or black, he produces in the colour unknown, and therefore incalculable, ratios of iron and cobalt, so that he cannot in advance see what the action will be, and must first acquire this knowledge by very considerable practice and skill. Moreover, since the alteration of the colour occurs only when it is fired, it will have a different appearance before as compared with after this operation. The painter, therefore, cannot, from the actual appearance of the colour, harmonise his picture, an evil which is particularly manifest in paintings reproducing the works of great masters."

The evil may be altogether obviated by the use of platinum grey, which is always easy to prepare, always produces the same shade, and, by reason of the large yield obtained from the platinum, is not very dear.

Grey may be also prepared from the metals, palladium and ruthenium, generally accompanying platinum. Of these the former gives a pale and ruthenium a redder grey, but the colours are too expensive.

Platinum Grey (Salvétat):—

Platinum powder (or else platinum chloride)	-	1 per cent.
Lead glass	- - - - -	3 "

are well mixed and finely ground. The lead glass is prepared by fusing

Minium	- - - - -	3 per cent.
Quartz sand	- - - - -	1 "
Borax glass	- - - - -	$\frac{1}{2}$ "

The grey obtained from *iridium* remains to be described. This colour is equally capable, with platinum grey, of resisting the action of fire, and also possesses all the good properties of the latter. It is, however, more expensive.

Iridium protosquioxide	- - -	1 per cent.
Zinc oxide	- - -	4 "
Grey flux	- - -	22 "

are thoroughly mixed and finely ground on a glass plate. In the inalterability of the iridium protos Sesquioxide reposes the property of this grey of mixing with all other colours without injuriously shading them, as happens with other greys.

The formation of *black* has already been described. To those unacquainted with the matter it would appear an easy thing to produce a good black, whereas actually this is one of the most difficult colours to prepare.

Black from Cobalt and Manganese :—

Calcined cobalt sulphate	-	-	-	2 per cent.
Dehydrated ferrous sulphate	-	-	-	2 „
Saltpetre	-	-	-	5 „

are mixed and exposed to a red heat in a Hessian crucible until the saltpetre is completely decomposed; the residue is washed with boiling water and the black powder (cobalt-manganese oxide) mixed and finely ground with grey flux in the proportion of 1: 2½.

Greyish Black :—

This recipe, frequently employed by the author (according to Salvétat's formula), gives very good results :—

Ferric oxide precipitated by ammonia	-	-	-	5 per cent.
Cobalt oxide	-	-	-	10 „
Salvétat's grey flux	-	-	-	85 „

Slightly fused in a crucible. Strong fusion makes the colour deep black.

Brownish Black (Bunel) :—

Ferric oxide precipitated by ammonia ¹	-	-	-	8 per cent.
Cobalt oxide	-	-	-	16 „
Salvétat's grey flux	-	-	-	76 „

treated as above. This blackish-brown colour may be

¹ This ferric oxide is obtained as hydrated oxide by precipitating a dilute solution of ferric nitrate or chloride by ammonia.

more easily obtained if, instead of 8 per cent. of the above ferric oxide, 4 per cent. of red and 4 per cent. of precipitated (by ammonia) ferric oxide be taken.

Deep Black :—

The following old French recipe can also be warmly recommended :—

Manganese oxide	-	-	-	-	19 per cent.
Saltpetre	-	-	-	-	59 „
Sand	-	-	-	-	19 „
Calcined borax	-	-	-	-	3 „
					100

These ingredients are mixed, fused and powdered ; then are taken

Above flux	-	-	-	-	15 per cent.
Cupric oxide	-	-	-	-	5 „
Commercial black enamel	-	-	-	-	80 „
					100

and ground up together, fused and poured out on to a sheet of metal.

Deep Black :—

According to Bunel, a beautiful colour for grounds is prepared from

Cupric oxide	-	-	-	-	9 per cent.
Grey flux	-	-	-	-	55 „
Calcined cobalt oxide	-	-	-	-	9 „
Manganese oxide	-	-	-	-	9 „
Soft light blue	-	-	-	-	18 „
					100

fused together. The black lends itself satisfactorily to admixture with other colours.

When fired on porcelain and examined microscopically this colour also reveals the cobalt-manganese oxide in a state of suspension—not solution—in the fused lead glass (flux).

In painting one often requires a very refractory black

(so-called "under work" black), which is not susceptible to attack from overlaid colours in the fusing. Such a black is prepared by simply mixing and grinding

Blue violet (gold preparation, p. 171)	-	-	5 per cent.
Cobalt-manganese oxide	-	-	$1\frac{2}{3}$ "
Zinc oxide	-	-	$1\frac{2}{3}$ "

The finest and most durable black is obtained from iridium, but this preparation is an expensive one.

Metallic iridium in the state of fine grey powder in which it is obtained in commerce (from Russia) is mixed with its own weight of decrepitated common salt and heated to slight redness in a porcelain tube, through which a current of chlorine gas is being passed. One part of the iridium is thereby converted into sodium irido-chloride, which is separated from the unaltered iridium by extraction with water. The aqueous solution of this double salt, evaporated to dryness along with sodium carbonate, and then extracted with water, leaves behind black iridium sesquioxide, which, when dried, is mixed with twice its weight of lead glass (prepared by fusing

Minium	-	-	-	-	-	12 per cent.
Quartz sand	-	-	-	-	-	3 "
Borax glass	-	-	-	-	-	1 ")

and finely ground on a glass plate. The iridium left unaltered by the first treatment with salt and chlorine is treated over again in the same manner.

If the iridium colour be examined under the microscope, when fired on porcelain, the iridium sesquioxide is found diffused unchanged throughout the clear fused lead glass.

Brongniart recommends for the production of an iridium black

Iridium oxide	-	-	-	-	-	$2\frac{1}{2}$ per cent.
Flux for grey	-	-	-	-	-	$7\frac{1}{2}$ "

Merely ground together. Iridium black may be mixed

with all other colours, especially reds, and completely preserves the shade of the colour with which it is blended, so that the latter remains perfectly pure and unaffected on firing.

All the colours hitherto described, including black, can be fired on biscuit porcelain, faience and stoneware at the temperature of the "retouching" fire (600° to 700° C.). If, however, they are to be fired at the first painting fire, one of the following fluxes—proposed by Salvétat for this purpose, and named by him A and B fluxes—is taken :—

A Flux :—

Minium	-	-	-	-	-	72 per cent.
Sand	-	-	-	-	-	22 „
Calcined borax	-	-	-	-	-	6 „
						100

B Flux :—

Minium	-	-	-	-	-	73 per cent.
Sand	-	-	-	-	-	24 „
Calcined borax	-	-	-	-	-	3 „
						100

We now come to the *white* colours, although, strictly considered, there is no white necessary for porcelain painting, the glaze being white, wherefore one has only to leave the glaze unpainted when white is required.

The white now described serves principally for marking out the lightest portions of the picture, where it is not feasible to effect this object by merely exposing the white surface of the porcelain. It is, moreover, frequently used for mixing in small proportions with the yellow and green pastes, to make them cover.

Cover White :—

Minium	-	-	-	-	-	1 per cent.
White sand	-	-	-	-	-	1 „
Crystallised boracic acid	-	-	-	-	-	1 „

are well mixed and fused in a porcelain crucible. This

enamel is endowed with the property of forming a clear colourless glass when cooled rapidly (*e.g.*, when poured into cold water), whereas when cooled slowly it becomes perfectly white and opaque. If the clear glass be heated to the fusing point it loses its transparency and becomes opaque as before. This property is shared by the enamels, whose opacity is developed by arsenic acid or tungstic acid. The opacity is presumably, in this case, caused by the separation of lead silicate, as it is in the white enamels by potassium arseniate or tungstate, or by tin oxide.

The solid matter is, however, in an infinitesimal state of division, since under the microscope merely a yellowish turbidity is visible, and even under the highest powers no individual particles can be detected.

Fire-resisting White :—

The composition of this enamel is perfectly analogous to that of the commercial white enamel, which can be brought into the desired condition by means of Rocaille flux.

This white enamel can be better prepared by mixing and fritting several times over

Sand -	-	-	-	-	-	53 per cent.
Tin— 15	} calcine	-	-	-	-	26
Lead—85		-	-	-	-	„
Potassium carbonate	-	-	-	-	-	21
						100

but only to incipient fusion, the mass being reground before being fritted anew. This proved recipe was formulated by Honoré.

The chemists Paris and Ami give the following prescription for producing a fire-resisting white :—

Sand -	-	-	-	-	-	45 per cent.
Minium -	-	-	-	-	-	37
Potassium carbonate	-	-	-	-	-	18
						100

This mixture is fused and serves for the formation of the following white:—

Above flux	-	-	-	-	-	68 per cent.
Calcined borax	-	-	-	-	-	14 „
Tin oxide	-	-	-	-	-	14 „
Arsenious acid	-	-	-	-	-	4 „
						100

This white is mostly used for touching up the lighter portions of white vestments, flowers, etc., which are not brought out sufficiently by the glaze alone; it can also be employed for those portions of a picture which have been overlooked by the painter in sketching, it being easy to mask any colours already applied, by covering them over with this white.

The so-called *Chinese white*, which is used in porcelain painting for the same purposes as white lead in oil painting, is produced by modifying white enamel with an admixture of Rocaille flux.

For strong fire and muffle firing this white is also used on soft porcelain and faience.

A white, or rather colourless, lead glass for applying to portions of the painting that have remained dull, as well as for mixing with colours that are too refractory, is obtained by fusing together

Minium	-	-	-	-	-	5 per cent.
White sand	-	-	-	-	-	2 „
Calcined borax	-	-	-	-	-	1 „

Brongniart prepared a *very fusible glaze* by simply mixing

Carminé flux	-	-	-	-	-	5 per cent.
Rocaille flux	-	-	-	-	-	1 „

As the glaze must be perfectly colourless, the employment of a very pure lead oxide is essential; if it contains copper, a fine white cannot be obtained (this applies also to the white described above). If the colour is to be rendered

more opaque, only a small proportion of the fire-resisting white should be taken.

2. HARD MUFFLE COLOURS.

The meaning of "hard" muffle colours has already been explained, as also the advantage derived from their use. The firing temperature is about 290° to 300° of the silver pyrometer.

To produce colours suitable for the requisite high temperature, it is only necessary to increase the refractory properties of the soft muffle colours by a previously determined quantitative addition of a metallic oxide, or, in other words, to decrease the percentage of flux by means of added oxides. Most of the hard muffle colours are used for ground work.

As a rule, it is sufficient to grind the ready-made soft muffle colour pastes, along with the oxides, on a glass plate, cobalt oxide alone requiring fusion. From what has gone before, it will be easy for any glass painter to harden the ready-made soft colours. Below a few additional recipes of Bunel's for this purpose are given:—

RED COLOURS:—

Orange Red.

Red (p. 153)	-	-	-	-	8 per cent.
Red ferric oxide	-	-	-	-	2 „

Blood Red.

Red (p. 153)	-	-	-	-	8 per cent.
Red ferric oxide	-	-	-	-	2 „

Violet Red.

Violet red (p. 170)	-	-	-	-	8 per cent.
Violet red ferric oxide	-	-	-	-	2 „

Dark Violet Red.

Dark red (pp. 153-154)	-	-	-	-	8 per cent.
Violet red ferric oxide	-	-	-	-	2 „

YELLOW COLOURS:—

Light Yellow.

Light yellow (p. 161)	-	-	-	8 per cent.
Oxide for same	-	-	-	2 „

Dark Yellow.

Dark yellow (p. 162)	-	-	-	8 per cent.
Oxide for same	-	-	-	2 „

YELLOW-BROWN COLOURS:—

Nankin Yellow.

Nankin yellow (p. 175)	-	-	-	$7\frac{1}{2}$ per cent.
Yellow ferric oxide	-	-	-	$1\frac{1}{4}$ „
Zinc oxide	-	-	-	$1\frac{1}{4}$ „

Ochre Yellow.

Ochre yellow (p. 175)	-	-	-	$7\frac{1}{2}$ per cent.
Yellow ferric oxide	-	-	-	$1\frac{1}{4}$ „
Zinc oxide	-	-	-	$1\frac{1}{4}$ „

Dark Brown Yellow.

Dark brown (p. 175)	-	-	-	$7\frac{1}{2}$ per cent.
Yellow ferric oxide	-	-	-	$1\frac{1}{4}$ „
Zinc oxide	-	-	-	$1\frac{1}{4}$ „

BROWN COLOURS:—

Sepia brown (p. 175)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

Reddish Brown.

Reddish brown (p. 174)	-	-	-	8 per cent.
Brown ferric oxide	-	-	-	2 „

Red Brown.

Red brown (p. 174)	-	-	-	8 per cent.
Brown ferric oxide	-	-	-	2 „

GREY COLOURS:—

Light Grey.

Light grey (p. 178)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

Bluish Grey.

Bluish grey (p. 177)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

Dark Grey.

Dark grey (p. 177)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

BLACKS :—

Greyish Black.

Greyish black (p. 180)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

Brownish Black.

Brownish black (p. 180)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

Deep Black.

Deep black (p. 181)	-	-	-	8 per cent.
Zinc oxide	-	-	-	2 „

BLUE COLOURS :—

Sky Blue.

Sky blue (p. 157)	-	-	-	8 per cent.
Zinc or cobalt oxide	-	-	-	2 „

Sky Blue.

Sky blue (p. 157)	-	-	-	8 per cent.
Zinc or cobalt oxide	-	-	-	2 „

GREEN COLOURS :—

Emerald Green.

Emerald green (p. 167)	-	-	-	7 $\frac{2}{3}$ per cent.
Oxide for emerald green	-	-	-	2 $\frac{1}{3}$ „

Bluish Green.

Bluish green (p. 165)	-	-	-	8 per cent.
Oxide for bluish green,	}	-	-	2 „
Naples yellow or zinc oxide				

The so-called Viennese enamels are analogous in composition to these hard muffle colours, but fuse at a somewhat lower temperature, *viz.*, about 275° of the silver pyrometer scale.

3. COLOURS FOR STRONG FIRE.

Colours that are capable of standing, without alteration, the heat of the kiln (about 140° Wedgwood) employed for firing the glazes are known as strong-fire colours. Naturally, the colours that will withstand such a high temperature are not very numerous. Cobalt oxide for blue, chromic oxide for green, uranium oxide for black, yellow from titanium oxide and brown from manganese-ferric oxide, or ferrous chromate, are the whole of the colours we can here employ for porcelain. For impure or soft porcelain, for which such high temperatures are not employed, very fine red and violet colours can be obtained from manganese, copper and ferric oxides. Moreover, for fine and ordinary faience, as also for stoneware, antimony oxide for yellow and copper oxide for green are also employed. Although the colours suitable for strong fire are relatively so few, they nevertheless present a decided advantage in that they may be gilded over without becoming softened thereby.

Since, as we have seen, the pigments—even those for strong fire—must be varied according as they are intended for true or biscuit porcelain, faience or stoneware, it becomes advisable, in the interests of perspicuity, to treat first of the true porcelain alone on account of the high temperature requisite for firing the glaze, subsequently discussing the soft porcelain, faience and stoneware all together.

(a) Colours for True Porcelain.

The colour most difficult to prepare in this case is blue, for which cobalt oxide alone is suitable. Even when the greatest care is exercised in the preparation of the cobalt oxide itself, as well as in the preparation of the colour paste, failures are numerous, chiefly manifested in spottiness, inequalities of colour and glazing and a granular and uneven

appearance of the porcelain throughout. Spots mostly result from insufficient or irregular firing; they are usually grey in colour, and always appear over a large extent of surface, but disappear for the most part on repeated sharp firing. The granular appearance, usually designated as "sputtering," is frequently due to the cobalt preparation having been laid on too thick (unequally).

This is fully treated of, along with the so-called "retraction" of the blue, in chapter xi.

It should be repeated that the accurate and careful preparation of the cobalt oxide constitutes the chief factor ensuring success.

Azure Blue.

Cobalt oxide	-	-	-	-	-	1 per cent.
Zinc oxide	-	-	-	-	-	12 „
Alum	-	-	-	-	-	2 „

The colour is applied to the biscuit before glazing.

Agate Blue.

A beautiful pale blue can be prepared in two different ways—either by applying direct (with the stippling brush) a thin layer of indigo blue (see below), or by preparing a mass from a little cobalt blue fused with one or two parts of glaze and grinding this with some thirty parts of glaze, finally sifting the product. The latter method is rather uncertain.

Green-blue shades are obtained by associating cobalt and chromic oxide with alumina. Cobalt oxide has double the colouring power of chromic oxide, so that with

Chromic oxide	-	-	-	-	-	4 per cent.
Cobalt oxide	-	-	-	-	-	2 „
Alumina	-	-	-	-	-	6 „

a blue can be prepared wherein the greenish tinge is but faint.

Mercurous chromate, although much dearer than chromic

oxide, will, when incorporated with water and cobalt oxide, and dried and ground, give much richer tones than can be obtained from chrome, since the latter cannot be so intimately mixed with the cobalt oxide.

Brongniart recommends the following method for producing greenish-blue colours with analogous oxides: One gram of dry cobalt carbonate is dissolved in hydrochloric acid and precipitated as cobalt hydrate by an excess of caustic potash, the precipitate being well washed in the usual manner and stored in a moist condition. On the other hand, ten grams of crystallised yellow potassium chromate are dissolved in distilled water, mixed with the hydrochloric acid and a little alcohol added. The mixture is set on the fire and raised to boiling, small portions of hydrochloric acid and alcohol being added so long as chlorine vapour is evolved. The solution is then removed from the fire, cooled down, and chromium hydrate thrown down by ammonia and thoroughly washed. The cobalt and chromic hydrates are mixed with a muller, dried and calcined over a strong fire. The method may be simplified by uniting the cobalt and chrome solutions and precipitating the hydrates together. However, since generally a certain definite shade of colour is to be produced and the proportion of the oxides is, in this event, difficult—if not impossible—to determine with accuracy, the original method is always to be preferred. These shades, when coated over with glaze, have a beautiful lustre, but the same effect cannot be obtained by applying the colour over the glaze.

Other important shades of colour can be obtained by mixing the aforesaid greenish-blue with magnesium carbonate.

A beautiful *turquoise blue* is prepared from

Green-blue (as above)	-	-	-	10 per cent.
Magnesium carbonate	-	-	-	3 „
Powdered glaze	-	-	-	10 „

An extensive variety of shades can be produced, accord-

ing to the firing temperature and the composition of the green-blue employed.

The blue most frequently used is the indigo blue prepared from cobalt oxide. This is a very pure shade of blue, which, however, is also most often subject to the accidents already referred to.

Brongniart recommends

Pure dry cobalt oxide	-	-	-	20	or	25 per cent.
Felspar for glaze	-	-	-	80	or	75 „
				100		100

If the cobalt oxide contains arsenic, 1 part of oxide and 2 parts of felspar can be taken, according to the same authority. Both substances are exposed to a strong fire, but in such a manner as to prevent fusion or boiling up, whereby a considerable loss in weight always results. The best way is to place the finely ground substances in a crucible, previously coated internally with a layer of fireclay, and set them in the furnace, since by this procedure the mass neither bubbles nor fuses. A reddish-blue agglomeration of the baked substance adherent to the bottom of the crucible, is obtained in this way.

A few glass painters employ for this purpose merely the rose-red powder of cobalt oxide met with in commerce. This may be applied direct on the glaze, but it is impossible to attain a perfectly pure fine indigo blue by this means.

It has already been mentioned that, for the preparation of green, only the chromic oxide that is used for green-blue should be employed. With this oxide a beautiful emerald green may be produced by simply applying the colour, without any admixture, direct to the glaze by a stippling brush in very thin and regular layers, or by applying it to the biscuit, incorporated with the glaze in which the latter is dipped, or, again, by coating the applied chromic oxide with

the glaze. It is advisable to employ a certain percentage of alumina along with the chromic oxide, as the colour is thereby rendered more stable. Generally 4 parts of alumina are taken to 6 parts of chromic oxide; magnesia also exercises the same influence. If chromic oxide be used alone, the green is generally of a brownish cast and resembles olive green. The application of zinc oxide to the chromic oxide produces apple-green colours.

All these greens, if laid on too thick or unevenly with the brush, exhibit a tendency to "sputter". Another combination of cobalt and zinc oxides with chromic oxide (the latter in excess) is employed for the production of a very brilliant bluish-green colour—*Seladon green*. According to Bunel, this very handsome colour is prepared by calcining

Cobalt oxide	-	-	-	-	-	10	per cent.
Zinc oxide	-	-	-	-	-	50	"
Of which mixture is taken	-	-	-	-	-	75	" with
Chromic oxide	-	-	-	-	-	25	"

The colour is stirred into the liquid porcelain glaze, 100 grams of colour being maintained in suspension in 20 litres of glaze whilst the piece to be glazed is being dipped. The shade of colour can, of course, be regulated by the proportion of the oxides taken.

Titanic Acid.

Titanic acid¹ is applicable for a few coloured glazes. The pure acid, mixed with a frit for under-glaze colouring, applied to calcareous stoneware and coated with lead glaze, gave a reddish-yellow, rutile a dark-yellow under-glaze colour of beautiful effect. However, rutile of various origin is unequal in colour tone, since it contains variable quantities of ferric oxide. Colour preparations of the pink type were produced.

¹ *Sprechaal*, 1891, p. 569.

The tin oxide was replaced by titanitic acid.

Titanic acid (pure)	-	-	-	-	50 parts.
Ground marble	-	-	-	-	25 „
„ quartz	-	-	-	-	18 „
Fused borax	-	-	-	-	4 „
Potassium bichromate	-	-	-	-	3 „

The mixture was finely ground and treated like pink. The result was a yellow-brown powder, as was also the case when rutile was substituted for pure titanitic acid. Both preparations, which were washed with water to remove the undecomposed residual potassium bichromate, yielded usable yellow-reddish-brown under-glaze colours, and gave similar majolica colours when mixed with majolica colour flux. Preparations containing larger proportions of titanitic acid gave somewhat darker tones.

Titanic acid or rutile, 99% _o	-	-	-	-	64 parts.
Ground marble	-	-	-	-	32 „
Potassium bichromate	-	-	-	-	4 „

These preparations may be mixed with the ordinary tin oxide pink colours and yield special red-violet under-glaze colours. If, in the yellow pigments prepared from tin oxide, antimonitic acid and lead oxide, the first named be replaced by titanitic acid or rutile, the result is equally an egg yellow, also applicable as an under-glaze colour, and—mixed with flux 1 : 9—as a majolica colour as well.

Yellow for strong-fire colours is prepared solely from titanitic acid, but even with this preparation the production of yellows is a difficult and uncertain matter; the products are straw-yellow in colour, with a strong reddish tinge. The metal titanium is obtained chiefly from rutile (red titanium shorl), occurring as reddish-brown, blood-red or even hyacinth-red crystal prisms. For our purposes rutile can be employed for the production of titanitic acid, unless it is preferred to obtain the acid in a pure state from some large

laboratory. The acid is prepared by fusing the elutriated rutile in a platinum crucible with three parts of potassium carbonate, extracting the excess of alkali with water until the latter begins to come through the filter turbid, and then dissolving the residual acid potassium titanate in concentrated hydrochloric acid. The titanitic acid is thrown down by boiling the diluted solution, whereby a portion of the acid remains dissolved along with iron and manganese. This portion of the acid may, however, be recovered by evaporating the solution and adding hydrochloric acid to the washings as soon as the latter pass through the filter milky. This portion of the acid is contaminated with traces of iron and manganese, which can, however, be removed by repeated boiling with hydrochloric acid, or preferably by digestion with ammonium sulphide, whereby the tin oxide, frequently present, is also got rid of, and sulphur, iron and manganese are formed, the titanitic acid being thereafter washed with very dilute hydrochloric acid. A more simple method is to calcine titanitic iron with sulphur in a Hessian crucible, then extracting the iron with hydrochloric acid, calcining the residue in a current of sulphuretted hydrogen, and extracting the residual iron with hydrochloric acid. Titanitic acid is white, turning to citron yellow when calcined, but again becoming white when cooled.

The yellow colours are obtained by mixing

Titanic acid	-	-	-	-	-	2½ per cent.
Felspar	-	-	-	-	-	7½ „

To prepare a special, fine *jonquil yellow* for strong fire, Arnoux of Toulouse employs a mixture of titanitic acid and tungstic acid, the latter being undoubtedly the cause of the peculiar tint of the colour. The preparation of this colour is, however, attended with considerable difficulties, especially as regards the production of a constant and pure tone.

Tungstic acid, a pale orange-yellow powder, is best obtained from a chemical laboratory. To prepare the acid oneself, metallic tungsten must be fused with potash and the filtered solution precipitated with nitric acid; the impure acid is dissolved in ammonium sulphide, the solution filtered and the yellow tungstic sulphide thrown down by nitric acid. The resulting yellow precipitate, which is somewhat soluble in pure water, is washed with a very little water, acidified with nitric acid, dried, gently roasted and calcined, a pale orange-yellow powder—tungstic acid—being thus obtained. By employing greater heat, or by prolonged exposure to sunlight, the acid becomes dark green, without any alteration occurring in the weight.

Through the influence of oxidising fumes the colour of the acid is immediately changed, a circumstance which should be borne in mind in porcelain painting.

Black and grey are also frequently required in addition to the blue, green and yellow shades. The finest deep black is obtained by means of uranium protoxide and porcelain glaze, in the proportion of 1 to 30. Manganese oxide, when used alone, does not give a fine black, but, on the other hand, a pure, brilliant blue-black is obtained by mixing and fusing cobalt and manganese oxides with a suitable quantity of porcelain glaze.

Iridium oxide imparts a greyish-black colour to the porcelain mass, but its use is attended with the drawback that the colour penetrates right through the porcelain and appears on the inside.

The various light and dark grey colours can be produced either by applying the above-named colours in more attenuated layers, or by employing dry platinum chloride. To this end, 50 parts (grams) of dry platinum chloride are used for light grey, 100 for medium and 150 for dark grey, and stirred up in 10 litres ($2\frac{1}{5}$ galls.) of liquid porcelain glaze, the ware being

dipped into the mixture. The same shades of grey can be produced if a solution of platinum chloride be prepared and applied to the biscuit; in this case also the colour frequently makes its appearance on the inner surface of the porcelain, which it colours with indefinite, dirty tints. Generally, a preliminary oiling will prevent this penetration of the colour.

Red porcelain colours for strong fire have not hitherto been successfully prepared, with the exception of a somewhat yellowish pale-red shade. Concentrated gold solution is alone used for preparing these various shades of colour. Bunel recommends the admixture of 20 to 30 grams of a concentrated gold solution with 10 litres of liquid porcelain glaze, into which mixture the ware is dipped. This method is, however, too expensive to be applied in practice. That proposed by Rouailler, who mixes

Gold solution	-	-	-	-	-	1 per cent.
Porcelain glaze	-	-	-	-	-	5 „
Alumina	-	-	-	-	-	5 „

well up together with a glass spatula, evaporates them to dryness and then calcines fairly strongly in a porcelain crucible, is cheaper. By grinding the mass on a glass plate a fine rose-red colour is obtained, and is applied by means of a stippling brush. The highly concentrated gold solution may also be applied direct to the biscuit, but, as the colour easily penetrates through, a preliminary oiling is advisable. By using weak solutions of gold, dirty violet shades are produced.

Whilst a very brilliant durable red is frequently encountered on Chinese porcelain ware, it is very difficult (if at all possible) for us to obtain the same in strong-fire colours. A very dark red—really a deep red-brown—is prepared from

Ferric oxide for red	-	-	-	-	2½ per cent.
Porcelain glaze	-	-	-	-	7½ „

well fused, ground fine, sifted and applied by dusting. Unfortunately, the colour never looks well when glazed.

Rose Dubarry.

By *Rose Dubarry* is understood a fine brilliant dark red gold colour—a purple—such as was peculiar to the products of Sèvres in the eighteenth century.

Stein prepared a so-called pink by calcining

Tin oxide	-	-	-	-	-	-	-	50
Marble	-	-	-	-	-	-	-	25
Quartz	-	-	-	-	-	-	-	18
Potassium bichromate	-	-	-	-	-	-	-	3
Borax	-	-	-	-	-	-	-	4

in the porcelain kiln. The resulting brownish-red colour was, when washed, mixed with ordinary porcelain glaze in various proportions and intimately incorporated therewith by grinding in a mill.

These coloured glazes were fused on to the porcelain by an oxidising fire, with good results, the colour of the glazes being a more or less intense pink, according to the proportions employed, but always tinged with a dark crimson-red coloration. For rose-coloured glazes these pink colours were unsuitable, and extensive experiments were therefore made to produce a pink that should give the desired tone. It was noticed that, concurrently with the diminution of the amount of lime in the mixture, the colour inclined more and more to a bluish tone; furthermore, that an increased ratio of boracic acid assisted this tendency considerably, and that pink perfectly free from lime could no longer be counted as among the red colours, pink rich in boracic acid and free from lime being quite lilac, both in itself and under stone-

ware glaze. A particularly fine *lilac* was furnished by pink prepared by fusing

Tin oxide	-	-	-	-	-	-	-	860
Borax	-	-	-	-	-	-	-	86
Potassium bichromate	-	-	-	-	-	-	-	54

strongly calcined in the porcelain kiln.

It was, moreover, observed that the colours containing an increased amount of calcium carbonate (chalk) assume a more reddish-brown shade, whilst those poor in lime incline towards rose. The colours rich in lime also faded more under stoneware glaze than those poor in this material. An increased addition of potassium chromate resulted in an increased extraction of the same in the washing (*i.e.*, undecomposed), without prejudicing the permanence of the colour under the glaze or appreciably influencing the shade. It was likewise found that an increase of boracic acid heightened the durability of the pink under glaze. The samples free from boracic acid, when calcined and washed, yielded dark brown-red colours, samples of which were mixed with porcelain glaze, with the result that the most suitable combination for producing pink was found to consist of 640 parts of tin oxide, 320 parts of marble and 40 parts of potassium bichromate. The white porcelain glaze employed was composed of 195 parts of marble, 337 parts of felspar, 307 parts of sand and 161 parts of Zettlitz earth. The samples yielded colours ranging from the most delicate rose to dark rose-red, according to the amount of the (boracic acid free) pink of the above-named composition, the proportions of colour to glaze for working on a large scale varying from 2 to 15 per cent. The glazes containing 8 to 10 per cent. of colouring matter exactly correspond to Rose Dubarry, as was proved by comparison with old specimens of Sèvres. It is necessary that the flame of the porcelain kiln employed for firing these glazes should be very clear and smokeless.

*Kaga Red.*¹

The Japanese province Kaga, or Kashin, of which Kanazawa is the chief town, is the centre of the manufacture of the Kutaniyaki, or Kaga porcelain. This porcelain is distinguished above all other Japanese ware by being painted with gold and a fine brightly coloured red enamel, known as Beni. H. Stein had occasion to examine this enamel and found

Silica -	-	-	-	-	-	-	-	28·01
Alumina -	-	-	-	-	-	-	-	1·91
Ferric oxide -	-	-	-	-	-	-	-	10·56
Lead oxide -	-	-	-	-	-	-	-	46·12
Potassium -	-	-	-	-	-	-	-	4·27
Sodium -	-	-	-	-	-	-	-	1·97
Loss in calcination -	-	-	-	-	-	-	-	7·38

It is, therefore, purely an iron colour, like the other Japanese enamels. The analysis of another red enamel from Arita, in the province of Hizen, revealed a similar composition also containing 10 per cent. of ferric oxide. The chief condition influencing the beauty of the colour is the fineness of the grinding. In preparing this red enamel, 10 to 15 parts of red ferric oxide and 90 to 95 parts of finely ground flux are intimately incorporated by grinding for several days. The flux is prepared by fusing

Minium -	-	-	-	-	-	-	-	574
Quartz -	-	-	-	-	-	-	-	334
Calcined soda -	-	-	-	-	-	-	-	92

The small proportion of alumina revealed by analysis can only be considered as an impurity or accidental admixture, and can, therefore, be left out of consideration. Another sample prepared in conformity with the analytical data of the red Arita enamel—which has the same proportion of red as the Kaga red, but a higher fusing point—gave, when finely milled, the same results as the Beni.

¹ *Sprechaal*, 1888, p. 393.

Copper Red and Watered Strong-fire Glazes.

Lauth and Dutailly¹ recommend a glaze rich in alkali, and containing a little lime and alumina; borax hinders the cracking or crazing, facilitated by alkalis in combination with alumina; the development of the red is furthered, not only by the alkalis, but also by the boracic acid acting as a solvent.

In order to preserve the copper from oxidation during the firing and cooling down, an addition of tin oxide is necessary, but the proportion of this addition must be subordinate to the copper. The employment of lead has produced only unsatisfactory results. The glaze is applied to the ware either by dipping the fired porcelain—sometimes glazed, sometimes not—or else by a brush to the glazed ware or biscuit. A small kiln of a capacity of 1·5 cubic metres and heated by a covering flame is used. The firing is carried on in a reducing atmosphere, and it has been found that the red develops most suitably in saggars to which air is admitted. The composition of the two glazes furnishing the best results corresponds to the subjoined proportions (copper, some 6 per cent., and tin deducted):—

I.	II.
67·02 per cent.	68·92 per cent. Si O ₂
7·06 ,,	6·85 ,, Al ₂ O ₃
7·83 ,,	17·83 ,, K Na O
9·87 ,,	6·39 ,, Ca O
8·23 ,,	— ,, B ₂ O ₃

agreeing with the following mixtures:—

I.	II.
40 parts	40 parts pegmatite
40 ,,	44 ,, sand
18 ,,	12 ,, chalk
12 ,,	— ,, calc. borax
— ,,	24·5 ,, soda
6 ,,	6 ,, cupric oxide
6 ,,	3 ,, tin oxide

¹ *Monit. Céram.*, vol. xix., p. 237.

Under the influence of an energetic reducing action, still further assisted by the presence of tin, the copper mixed with the glaze is brought to the metallic state by the high temperature employed. When the constitution of the glaze permits, the metal becomes dissolved, the solution being complete, provided the content of copper is not too high. If the copper solution be cooled under certain conditions, especially when the operation is effected suddenly, the glaze is converted into a colourless glass, which is, however, capable of re-conversion to red on exposure to moderate heat; on the other hand, if the cooling proceeds slowly, the red develops with its full lustre and transparency.

If, however, the glaze is so constituted that the copper is insoluble therein, or should the amount of metal be too large, separation occurs at the instant of cooling, the very finely divided metallic powder appearing as an opaque colour.

Pink Red for Majolica Glaze.

A suitable pink preparation can be produced by finely grinding 1 part of potassium bichromate in a basin with a little water and alcohol, adding by degrees 8 parts of powdered marble and 16·5 parts of pure tin oxide, and intimately incorporating the now almost dry mass. This mixture is spread to a depth of $1\frac{1}{4}$ to $1\frac{1}{2}$ inches in flat, unglazed trays, placed in a capsule and exposed to a majolica or stoneware firing heat. The resulting brown-violet mass is washed with water containing a little hydrochloric acid, dried, calcined a second time in the kiln and again washed repeatedly. The following mixture serves for dilution: 2 parts of pure tin oxide, 2 parts of very finely ground quartz, 1 part of ground marble or washed chalk, mixed and also exposed to a clear majolica or stoneware fire, in suitable vessels.

Dark red is obtained from 5 parts of the dry pink prepara-

tion and 7 parts of the above mixture, finely ground in a mill, rewashed and dried. The resulting pale violet preparation should be used at once for majolica.

If intended for a ground colour, and, therefore, having to cover better, only 5 to 6 parts of the flux are taken to 5 parts of the pink.

Purple: 8 parts of dark red and 1 part of pure cobalt oxide, finely ground. *Cardinal red*: 12 parts of dark red and 1 part of cobalt bicarbonate. The majolica flux is made from an intimate mixture of 22·5 parts of quartz flour, 18·5 parts of crystallised borax, 30·5 parts of minium, 16·5 parts of ground felspar, 5 parts of kaolin and 7 parts of washed chalk.

In order to fit the above-named *dark-red preparation* for red stoneware glaze or strong-fire colour for stoneware, it is exposed to a clear furnace fire, whereby it acquires a fine light-red colour.

A *dark-red* glaze can be prepared from 70 parts of stoneware glaze frit, 15 parts of minium, 15 parts of felspar and 10 to 12 parts of calcined dark red. The stoneware glaze frit is made from 25 parts of minium, 35 parts of quartz flour, 10 parts of crystallised borax, 12 parts of kaolin and 18 parts of washed chalk.

Brown tones are prepared in a great variety of shades. A beautiful *chestnut brown* is obtained as follows :—

Ferrous chromate	-	-	-	-	8 per cent.
Chromic oxide	-	-	-	-	2 „
Liquid porcelain glaze	-	-	-	-	5 „

Mixed and finished by grinding with a sufficient quantity of suitable porcelain glaze.

By adding a little manganese oxide to the above mixture the colour may be shaded into *chocolate*. Very dark brown tints may be produced by substituting ferric oxide or cobalt oxide for the chromic oxide.

Umber also makes a beautiful brown, which, however, must not be exposed to too strong a fire. Nevertheless, it is generally fired rather strongly, whereby the colour is made unequal, and instead of one colour, several—such as pale yellow, light brown and dark brown—are produced in great variety. In short, the porcelain is quite marbled, and as the shades are appropriate, the colour produced in this way is generally named “tortoise shell,” and is frequently prepared. Brongniart recommends the following formula :—

Manganese oxide	-	-	-	-	15 per cent.
Umber	-	-	-	-	20 ”
Porcelain glaze	-	-	-	-	65 ”

Before proceeding to mix the above substances, the umber should be calcined ; all are then ground together, sifted and fused. The mass, not too finely powdered, is applied by dusting.

Preparation of Coloured Glazes for Porcelain, according to H. Stein.¹

This authority recommends readily fusible glazes for which lighter bodies, such as the Chinese and Japanese, should be used. Equal fusibility of all the coloured glazes is also necessary, of course, since the altered fusibility caused by the simple admixture of the pigmentary metallic oxides to form colourless glazes, would result in the association of well-fused glazes, with underdone and over-fused glazes in the same batch, and even on the same piece when coated with several glazes.

The metallic oxides are also fluxes, and in the case of highly coloured glazes the alteration of fusibility effected by the large proportion of the (merely mixed) pigmentary oxides, is also considerable. It is, however, not difficult to equalise the fusibility of the whole of the coloured glazes by

¹ *Sprechsaal*, 1888, pp. 506, 825.

omitting from the uncoloured glaze an amount of flux corresponding chemically to the metallic oxide employed. For cobalt oxide, cupric oxide and nickel oxide, marble (calcium carbonate) is omitted from the glaze at the rate of 100 parts of marble to 83 parts of cobalt oxide, 79·4 of cupric oxide, or 75 of nickel protoxide. For ferric oxide, manganese oxide, chromic oxide and uranium oxide, alumina is left out of the glaze at the rate of 103 parts of alumina for 160 of ferric oxide, 158 of manganese oxide, 153 of chromic oxide and 288 of uranium oxide.

The following mixture gives a colourless glaze :—

Felspar -	-	-	-	-	-	-	-	314
Quartz -	-	-	-	-	-	-	-	470
Marble -	-	-	-	-	-	-	-	137
Porcelain earth	-	-	-	-	-	-	-	79

Blue glaze should contain 4 per cent. of cobalt protoxide, *i.e.*, 40 parts per 1000 of glaze. Now, since 100 parts of marble are equivalent to 75 parts of cobalt protoxide, 53 parts of marble should be omitted from the glaze to compensate for the 40 parts of cobalt protoxide, so that instead of 137 parts of marble only 84 should be taken. The 40 parts of cobalt protoxide are obtained by dissolving 44 parts of cobalt oxide in hydrochloric acid, an excess of acid being, as far as possible, avoided.

The resulting solution, containing the desired 40 parts of cobalt protoxide, is largely diluted with water and mixed with the finely divided glaze mass, or a portion thereof. The mixture is then warmed and stirred, whilst a thin stream of strong soda solution is poured in so long as effervescence continues and red litmus paper is not turned blue. The precipitation is complete as soon as the solution does change the colour of red litmus, and, thereupon, the whole is transferred to a large vessel, and a large volume of water added to wash the glaze. After being well stirred up the liquid is left at rest for some

time, until the intimately mixed precipitate and glaze have settled down and the supernatant liquid appears clear. The latter is then decanted with care and replaced by a fresh quantity of water which is well stirred up with the sediment, the operation being, as a rule, complete after this procedure has been repeated some five or six times, the attainment of the end being indicated by the absence of reaction upon red litmus paper. Thorough washing is necessary for the removal of the injurious salt (common salt) proceeding from the glaze and present in the liquid after the process of precipitation. The finally resulting (gruelly) glaze is somewhat slinky, and it is advisable, in order to obviate this injurious characteristic, to dry the mass and mix the dry material with the portions of ground glaze at hand, incorporating them together by grinding for a short time. The glaze prepared in this manner has the same fusing point as in the uncoloured state, and the two may therefore be fired at the same temperature. The blue glaze is perfect, especially when fired in an oxidising flame and with a wood fire, and far surpasses any eighteenth century product, the valued tinge of purple being, moreover, not lacking. The sea-green glazes (Seladon) of Chinese porcelain are coloured green by cupric oxide, of which from 0.5 to 2 per cent. was found on analysing a number of such glazes. The preparation of similar Seladon glazes by means of the above-named formula and 2 per cent. of cupric oxide can be effected by omitting from the glaze 25 parts of marble for the 20 parts of cupric oxide (79.4 of cupric oxide being equivalent to 100 of marble), *i.e.*, by taking only 112 instead of 137 parts of marble.

(b) Colours for Biscuit Porcelain, Faience and Stoneware.

The colours we are now considering are less suitable for painting than for colouring the entire mass. True porcelain is the most difficult to colour in the mass, and in fact only

one pigment—cobalt oxide—capable of thus colouring it an unalterable and beautiful pale blue, is as yet known. True porcelain is, however, very seldom coloured through and through.

On the other hand, nearly every kind of colouring matter is employed to colour biscuit porcelain, the fine kinds of faience, and stoneware, in the mass: the colours to be produced will come out so much the finer in proportion to the vitreous character of the mass to be coloured. Biscuit porcelain and fine English stoneware, which contain a large amount of vitreous materials; develop the finest colours. On the other hand, faience ware containing much less vitrifiable constituents, requires the colours to be fritted before admixture.

The colouring of faience and stoneware masses can be effected by the same process. The former ware is only coloured in yellow, brown, and black-shades.

Very Pure Black for Stoneware (Aikin).

Plastic clay	-	-	-	-	-	48 per cent.
Kaolin	-	-	-	-	-	2 „
Calcined ochre	-	-	-	-	-	43 „
Manganese oxide	-	-	-	-	-	7 „
						100

Egyptian Brown (Shaw).

Plastic clay	-	-	-	-	-	48 per cent.
Black marl	-	-	-	-	-	14 „
Calcined ochre	-	-	-	-	-	30 „
Manganese oxide	-	-	-	-	-	8 „
						100

In both these recipes the mass must be reduced to a very fine powder whereby a higher degree of plasticity is acquired and the work is greatly facilitated.

Brongniart gives this composition (for stoneware mass) as a basis for the following colorations:—

Very white plastic clay	-	-	-	70 per cent.
Porcelain biscuit	-	-	-	25 „
Calcined gypsum	-	-	-	5 „
				100

In place of gypsum, quartzose porcelain earth may be taken. For the production of a *pale blue* it is only necessary to mix the basis (white stoneware body) with 0.05 part of cobalt oxide. A deep bright blue can be prepared from the above-named basis with the addition of

Alkali	•	-	-	-	1.2 per cent.
Cobalt oxide	-	-	-	-	$\frac{1}{10}$ „

Ordinary blue stoneware is seldom coloured through and through, but only coated over with a thin layer of blue mass.

Pale green is obtained by mixing the basis with 0.05 part of chromic oxide; *bluish green* with basis and

Cobalt oxide	-	-	-	-	0.03 part.
Chromic oxide	-	-	-	-	0.03 „

Dark greens by addition of

Chromic oxide	-	-	-	-	0.01 part.
---------------	---	---	---	---	------------

to the mass.

Beautiful, pure *yellow colorations* are produced by means of a lead glaze.

The colouring of fine stoneware (as also of true porcelain) necessitates considerably modified methods of combination. The white mass forming the basis is made up of

Quartzose kaolin	-	-	-	-	48 per cent.
Pure plastic clay	-	-	-	-	16 „
Pure quartz sand	-	-	-	-	16 „
Porcelain glaze	-	-	-	-	16 „
Calcium carbonate	-	-	-	-	4 „
				100	

The various pigments are mixed with this basis.

Blue (Salvétat).

Basis	-	-	-	-	-	90 or 70 per cent.
Blue for strong fire	-	-	-	-	-	10 „ 20 „
White plastic clay	-	-	-	-	-	— 10 „
						100 100

The mass remains blue under the glaze.

Pale Blue.

Basis	-	-	-	-	-	95 per cent.
Cobalt oxide	-	-	-	-	-	5 „
						100

This mass is designated *agate* on account of its colour.

Blueing Stoneware Mass with Cobalt Salts.

A solution (about 1 : 2) of cobaltous nitrate or sulphate in water is prepared. 1 kilogram of cobalt nitrate and 2 litres of water yield 2480 cubic centimetres of cobalt solution. 230 c.c. of ammonia, of the prescribed strength, are required to precipitate each 1000 c.c. of the above solution. The solution, measured at the rate of 1 kilo. of the solid salt to each 1000 kilos. of stoneware mass, is poured into the mixing vat, and after a short time a measured quantity of ammonia—570 c.c. per 1 kilo. of the salt—is added. The whole of the cobalt protoxide is thrown down in a more finely divided condition than can ever be attained by mechanical means, and is equally distributed throughout the sedimental mass.

Green.

Basis	-	-	-	-	-	85 or 85 per cent.
Blue for strong fire	-	-	-	-	-	5 „ 10 „
Chromic oxide	-	-	-	-	-	10 „ 5 „
						100 100

The coloured mass also preserves its fine green tone when glazed.

Bluish Green.

The following oxides are first combined :—

Chromic oxide	-	-	-	-	50	per cent.
Cobalt oxide	-	-	-	-	25	„
Zinc oxide	-	-	-	-	25	„
					100	

and then mixed—to produce the bluish-green coloration—as follows :—

Above oxide mass	-	-	10	or	5	per cent.
Basis	-	-	90	„	95	„
			100		100	

The full brightness of the colour is developed only on glazing.

Brown.

Basis	-	-	-	-	80	or	85	per cent.
Calcined ferric oxide	-	-	-	-	20	„	15	„
					100		100	

The mass must be well washed by sedimentation after careful mixing.

Olive Green (Bronze).

Basis	-	-	-	-	-	88	per cent.
Calcined nickel oxide	-	-	-	-	-	10	„
Cobalt oxide	-	-	-	-	-	2	„

Nickel oxide may be purchased from any large laboratory. This pigment is not greatly to be recommended, the result being always uncertain. Sometimes very fine pure colours are obtained, whilst at others they are dark and dirty. Owing to this element of uncertainty, this colour is but very rarely used for masses.

Rose-red and purple masses are produced with purple of Cassius. According to Brongniart, the white mass (basis) is mixed and stirred up with the solution of gold described

for purple on p. 73, the purple being precipitated by a solution of tin, added drop by drop. The addition of chalk is made only after the coloured mass has been well washed. By altering the proportion of purple or mass, various shades may be obtained, which behave very well under glaze.

Yellow (Pale Tint).

Basis	-	-	-	-	-	-	95 per cent.
Rutile (see p. 194)	-	-	-	-	-	-	5 „
							100

Yellow (Flesh Tint).

Basis	-	-	-	-	-	-	90 per cent.
Rutile	-	-	-	-	-	-	10 „
							100

The coloured mass will not bear glaze.

Grey.

Basis	-	-	-	-	-	-	97½ per cent.
Rutile	-	-	-	-	-	-	2½ „

This mass will also preserve its colour under glaze.

Black Brown.

Ferrous chromate	-	-	-	-	-	-	14 per cent.
Cobalt oxide	-	-	-	-	-	-	14 „
Manganese oxide	-	-	-	-	-	-	14 „
Basis	-	-	-	-	-	-	58 „
							100

The above materials are fritted together and calcined in the strong fire of the porcelain kiln. Variations in shade may be produced by modifying the quantitative proportions.

Black.

Basis	-	-	-	-	-	-	91 per cent.
Calcined ferric oxide	-	-	-	-	-	-	5½ „
„ cobalt oxide	-	-	-	-	-	-	3½ „

This black generally fulfils its purpose : if a more durable black is required, uranium oxide should be employed.

Finally, a few recipes for colouring biscuit porcelain in the mass, as prescribed by the French manufacturer Tribouillet, are given below. The following basis is employed for the white mass :—

White porcelain biscuit	-	-	-	30 per cent.
Quartzose porcelain earth	-	-	-	10 "
Very white plastic clay	-	-	-	60 "
				100

Pale Green.

Above basis	-	-	-	-	90 per cent.
Lead chromate	-	-	-	-	5 "
Sand	-	-	-	-	5 "

ground up. The proportion of sand may be increased, since it serves to counteract the increased fusibility imparted by the lead salt.

Citron Yellow.

The following are fritted at moderate heat :—

Antimony oxide	-	-	-	-	5 $\frac{3}{4}$ per cent.
Minium	-	-	-	-	5 "
Sand	-	-	-	-	1 $\frac{1}{4}$ "

To prepare the mass

Above frit	-	-	-	-	7 $\frac{1}{4}$ per cent.
White porcelain mass	-	-	-	-	85 $\frac{1}{2}$ "
Porcelain biscuit	-	-	-	-	7 $\frac{1}{4}$ "
					100

are intimately mixed.

Nankin Yellow.

In preparing this colour a frit is made of

Antimony oxide	-	-	-	-	23 $\frac{1}{2}$ per cent.
Red ferric oxide	-	-	-	-	11 $\frac{3}{4}$ "
Minium	-	-	-	-	47 $\frac{1}{4}$ "
Sand	-	-	-	-	17 $\frac{1}{2}$ "

and mixed with white porcelain mass and biscuit, in the same proportions as are employed in the case of citron yellow.

Turquoise Blue.

This highly-appreciated colour can be advantageously prepared according to the subjoined recipe :—

Cupric oxide	-	-	-	-	5 $\frac{3}{4}$	per cent.
Anhydrous sodium carbonate	-	-	-	-	17 $\frac{3}{4}$	„
Sand	-	-	-	-	76 $\frac{1}{2}$	„

fritted at not too high a temperature (cupric oxide being, as is well known, rather volatile).

Of the above frit

					59 $\frac{1}{4}$	per cent. is mixed with
White porcelain frit	-	-	-	-	14 $\frac{3}{4}$	„
Washed marl	-	-	-	-	11 $\frac{1}{4}$	„
Chalk	-	-	-	-	14 $\frac{3}{4}$	„
					100	

well mixed: the admixture of organic substances is here inadmissible, and an oxidising flame should alone be employed for the firing.

Turquoise enamel is prepared from

Sand	-	-	-	-	-	47·14	per cent.
Minium	-	-	-	-	-	23·58	„
Sodium carbonate	-	-	-	-	-	11·79	„
Saltpetre	-	-	-	-	-	12·76	„
Cupric oxide	-	-	-	-	-	4·71	„

For applying the glaze to the porcelain the old practice of sprinkling followed in Vincennes is advisable, and probably also the so-called injection method. The use of any kind of adhesive material, such as fat, turpentine, glycerine or gum, must be avoided, since the glaze fuses, even before they are completely burnt off, and then encloses reducing substances which blacken both the fundamental mass and the covering layer. Turquoise enamel gives a finer tone when applied on white glaze than if applied to the biscuit direct without any intermediate layer.

To produce blue colours, 1 to 4 per cent.—according to

the shade desired—of cobalt oxide is added to the ordinary white frit, and the mixture fritted anew; the marl and chalk being thereafter added in the usual (above-named) proportion.

Violet shades are most effectively coloured with manganese oxide, most beautiful shadings being obtained by the addition of a little cobalt oxide to the frit.

Manganese oxide - - - -	5½ per cent.
Anhydrous sodium carbonate - -	16½ "
Saltpetre - - - -	5½ "
Sand - - - -	72¼ "
	100

The violet mass is prepared from

Above frit - - - -	77 per cent.
Chalk - - - -	11½ "
Washed marl - - - -	11½ "
	100

Black.

The various degrees of black may be produced by mixing the violet colours with sulphur and ferric oxide.

Biscuit porcelain is not always coloured throughout the entire mass, the colour being restricted to a thin surface layer ($\frac{1}{2}$ centimetre = $\frac{1}{8}$ inch) applied over the white body, and it is then possible to ornament it in various ways with any other colours desired.

According to G. Steinbrecht,¹ red under-glaze colours on stoneware are particularly liable to crack off, besides being difficult to apply, by reason of the presence of tin oxide. The constitution of the furnace gases is of less importance than the composition of the mixture, in determining the colour, as is shown by the subjoined recipes for green and red.

¹ *Sprechaal*, 1891, p. 123.

Green.

Chromic oxide	-	-	-	-	-	20 parts,
Flux	-	-	-	-	-	40 „
Calcined silica	-	-	-	-	-	40 „

The flux consists of 30 parts of silica, 15 parts of borax, and 1 part of chalk.

Red.

Chromic oxide	-	-	-	-	-	1 part.
Tin oxide	-	-	-	-	-	48 „
Flint	-	-	-	-	-	19 „
Calc spar	-	-	-	-	-	20 „
Gypsum	-	-	-	-	-	10 „
Sodium bicarbonate	-	-	-	-	-	2 „

The following mixture requires a not too strong fritting heat :—

Tin oxide	-	-	-	-	-	26 parts.
Chalk	-	-	-	-	-	40 „
Sand	-	-	-	-	-	17 „
Potassium chromate	-	-	-	-	-	1.5 „
Borax	-	-	-	-	-	15.5 „

This, by reason of its sintering properties, exhibits no tendency to splinter and will stand a strong heat without damage to the clearness of the design. The attainment of a deeper red tone is dependent on the increase of the percentage of potassium chromate.

CHAPTER VIII.

THE ENAMEL COLOURS.

THE enamel itself has already been thoroughly discussed. The first observation to be made at present is that enamel colours are divided into two broad classes—transparent and opaque—which are known respectively as transenamel and openamel, for short. Now-a-days, almost any desired colours can be imparted to enamels, and those employed for porcelain are, as a rule, imitated in the present instance.

White enamel, which is always opaque and communicates this peculiarity to all the colours with which it is mixed, is prepared with tin or zinc oxide. The coloured transenamels differ from the preceding in that the colouring metallic oxides are completely dissolved in the flux, on which account they are transparent, unless, purposely, deprived of this characteristic by the addition of tin oxide.

Enamels can be employed for hard felspar porcelain, as well as for faience, stoneware, porcelain, biscuit, glass and metals. The oxides occur in the coloured enamels as silicates or borates, and the fusing point of these colours varies considerably, being high in the case of true glasses—fusing only at about 1200° C.—and low in the case of enamels for light glazes on porcelain biscuit in imitation of faience—about 900° C. The enamels intended for actual glass painting and for metal, fuse at still lower temperatures; those for metal contain, of course, a very large amount of lead oxide.

An ordinary colourless transenamel is obtained from

Quartz	100	per cent.
Fused borax;	50	"
Minium	200	"

A transparent enamel resembling ivory is prepared by means of the following combination :—

Quartz	31	per cent.
Fused borax	15½	"
Minium	60½	"
Potassium antimoniate	1	per cent.
Hydrated ferric oxide	2	"
Flowers of zinc	1	"

Subjoined are a few recipes for preparing transenamels :—

Yellow.¹

Quartz	160	per cent.
Borax	50	"
Minium	200	"
Potassium chromate	2	"

Yellow Brown.

Quartz sand	100	per cent.
Borax	50	"
Minium	200	"
Red ferric oxide	40	"

Green.

Quartz	100	per cent.
Borax	50	"
Minium	200	"
Cupric oxide	10	"

Blue.

Quartz	100	per cent.
Borax	50	"
Minium	200	"
Cobalt oxide	6	"

¹ The following recipes are also suitable for employment as coloured glazes for porcelain biscuit.

Violet.

Quartz	-	-	-	-	-	100 per cent.
Borax	-	-	-	-	-	50 "
Minium	-	-	-	-	-	200 "
Manganese carbonate	-	-	-	-	-	12 "

Grey.

Quartz	-	-	-	-	-	100 per cent.
Borax	-	-	-	-	-	50 "
Minium	-	-	-	-	-	200 "
Cobalt oxide	-	-	-	-	-	$\frac{1}{4}$ "
Cupric oxide	-	-	-	-	-	1 "
Manganese oxide	-	-	-	-	-	1 "
Red ferric oxide	-	-	-	-	-	1 "

Black.

Quartz	-	-	-	-	-	100 per cent.
Borax	-	-	-	-	-	50 "
Minium	-	-	-	-	-	200 "
Cobalt oxide	-	-	-	-	-	1 "
Cupric oxide	-	-	-	-	-	1 "
Manganese oxide	-	-	-	-	-	3 "
Red ferric oxide	-	-	-	-	-	2 "

All these coloured enamels are transparent; they may, however, be immediately converted into the opaque condition by the addition of a suitable amount of tin oxide. Now, as it is known that the enamels acquire a certain degree of opacity when the tin oxide exceeds one-tenth of the entire weight, it is merely necessary to add this proportion of tin oxide. Salvétat advises the use of calcine which he prepared from an alloy of

Lead	-	-	-	-	-	6 per cent.
Tin	-	-	-	-	-	1 "

and uses 106 parts of this instead of 100 parts of minium.

A few recipes by Bastenaire d'Audenard for enamelled faience are given below, that marked *a* being the harder (containing the most tin), and *b* the softer (containing the most lead). The temperature necessary for fusion is 60° to 70° Wedgwood; on account of the constant presence

of organic substances, such as carbon, it is necessary to fuse two or three times over, in order to produce a perfectly white enamel. Of course all these products are opaque.

(a) Calcine { Tin oxide - - 23 } 45 per cent.
 { Lead oxide - - 77 }

100

Quartz sand - . - - . 45 per cent.

Minium - - - - - 2 „

Sea salt - - - - - 5 „

Soda - - - - - 3 „

100

(b) Calcine { Tin oxide - - 18 } 45 per cent.
 { Lead oxide - - 82 }

100

Quartz sand - - - - - 45 per cent.

Sea salt - . - - - 7 „

Soda - - - - - 3 „

100

These white enamels (*a* or *b*, according to the object in view) are coloured as follows:—

Yellow.

White enamel 91 per cent.

Antimony oxide - - - - 9 „

100

Blue.

White enamel 95 per cent.

Sky blue - - - - - 5 „

100

Green.

White enamel - - - - 95 per cent.

Copper scale - - - - 5 „

100

Pistachio Green.

White enamel	-	-	-	-	94	per cent.
Cuprous oxide	-	-	-	-	4	„
Antimony oxide	-	-	-	-	2	„
					100	

Violet.

White enamel	-	-	-	-	96	per cent.
Manganese oxide	-	-	-	-	4	„
					100	

The colouring matter is either simply mixed with the finely-ground enamel or fused along with the latter, according to the requirements of the case.

The operation of enamelling is performed by dipping the piece of faience in the coloured enamel—stirred up to form a thin gruel—so as to cover the external surface, the piece being held fast from the inside. Only when the outside is dry enough to hold is the enamel applied to the inside surface: this is done by pouring in a spoonful of white enamel, turning the piece round and round until the surface is coated, and then pouring the excess away. Generally when the piece is dipped, some enamel attaches itself to the bottom (outside), and this has to be removed by brushing before the ware is fired, to prevent it fusing and causing the piece to stick to the support. This work, by reason of the dust produced, is very injurious to the health of the work-people.

In firing enamelled ware care must be taken to keep white pieces apart from green or blue ware, since the colours of the latter, being readily volatilised, will tarnish the former.

Th. Deck¹ gives the following recipes for producing transparent coloured enamels on stoneware:—

¹ *La Faience*, Paris, 1887.

1. *Flux or Transparent Glaze.*

	(a) Hard.	(b) Soft.
Minium (chemically pure) -	30	35 per cent.
Quartz sand (purest) -	50	45 "
Potash - - - - -	12	12 "
Sand - - - - -	8	8 "
	100	100

2. *Lapis Lazuli Blue.*

Flux - - - - -	95 per cent.
Cobalt oxide - - - - -	0.7 "
Cupric oxide - - - - -	4.3 "
	100

3. *Turquoise Blue.*

Flux - - - - -	93 per cent.
Cupric oxide - - - - -	7 "
	100

4. (a) *Green.*

Sand - - - - -	35 per cent.
Minium - - - - -	55 "
Potash - - - - -	5 "
Borax - - - - -	5 "
Cupric oxide - - - - -	4 "

4. (b) *Green (Watery).*

Sand - - - - -	30 per cent.
Minium - - - - -	55 "
Potash - - - - -	10 "
Borax - - - - -	5 "
Cupric oxide - - - - -	4 "

5. *Camelia Green.*

Flux - - - - -	45 per cent.
Cupric oxide - - - - -	5 "
Ferric oxide - - - - -	5 "
Sand - - - - -	20 "
Minium - - - - -	25 "
	100

12. *Ivory Yellow.*

Flux	-	-	-	-	-	52 per cent.
Ferric oxide	-	-	-	-	-	3 „
Sand	-	-	-	-	-	20 „
Minium	-	-	-	-	-	25 „
						100

13. *Garnet Red.*

Flux	-	-	-	-	-	82 per cent.
Manganese oxide	-	-	-	-	-	6 „
Antimony oxide	-	-	-	-	-	2 „
Soda	-	-	-	-	-	5 „
Saltpetre	-	-	-	-	-	5 „
						100

These mixtures are fused in good Hessian crucibles, then poured out and finely ground. The number of coloured glazes may be easily increased by employing the simple formulæ with further colouring oxides, and the shades of the individual glazes can be made lighter by increasing the proportion of the flux, *i.e.*, clear glaze.

Enamels for Artistic Work.

In many art industries, as for example gold-working and the manufacture of bronzes, enamels are employed for purposes of ornamentation and for entire pictures. The enamel masses here used vary in composition and application but little from those just described for industrial employment, the difference mainly consisting in the necessity for using only the finest materials, since it is by these alone that the production of handsome coloured enamels is possible. The increased cost entailed thereby is a minor consideration, owing to the very small quantity of enamel required for these purposes.

As the enamels employed for artistic purposes do not need to be specially capable of resistance, chemically speaking, they are usually composed with a view to ready

fusibility, since it is easier in such case to apply any determined colour and preserve its beauty when fired.

The knowledge of the constitution of enamels being now-a-days general, manufacturers whose products enjoy a specially high reputation—such as the enamel makers of Venice—can easily maintain their unimpeachable purity by bearing in mind the factors just mentioned.

Enamel masses of very low fusing point may be prepared by employing glass masses rich in lead, and these may be used with impunity for the purposes in question, since their low power of resistance will not have any unfavourable results. Below are given particulars of the composition of enamel masses which have proved reliable for various artistic purposes, and which may be employed in various ways. The mass may be either fused on at a single operation, or the object may be first covered with a layer of white mass by fusion and the coloured enamels applied thereon by repeated fusings. For single colour enamels only one fusing is usually performed, but in cases where it is a question of producing enamel paintings, the object is first coated with a white enamel mass which serves as a ground for the subsequent painting.

White Enamels for Jewellery.

Two parts of tin and 1 of lead are calcined and completely converted into oxides: 1 part of this oxide mixture is mixed with 2 parts of powdered white crystal glass and fused in small crucibles along with a very small amount of saltpetre or manganese oxide, to act as a decolorant; the mass being thereafter poured out into cold water. Fusion is repeated twice or three times—in many instances even four times, and in fact must be continued until the enamel no longer appears bladdery, but perfectly homogeneous. After it has been ground to a fine powder it may be applied either

by itself, or, for small surfaces, mixed with oil of lavender and laid on with a brush like oil colours.

If white enamel of still lower fusing point is desired the following materials may be employed :—

Tin-lead oxide	-	-	-	-	100 parts.
Pure quartz flour	-	-	-	-	60 „
Common salt	-	-	-	-	25 „

In place of pure quartz flour, sand may also be used, but requires to be subjected to a special process of purification if a pure white product is to be obtained. To this end 100 parts of sand are calcined with 25 parts of common salt. The iron present in the sand combines with the chlorine in the salt to form a compound which volatilises at the temperature employed, leaving behind a fritted product sufficiently free from iron. The sand is then mixed with 25 parts of pure minium and fused, thus producing a fritted mass of lead-soda glass.

To produce enamels from this mass it is powdered very fine and mixed with pure tin oxide, or with the mixture of tin and lead oxides, at the rate of 100 parts of oxide to 50 parts of the frit. The larger the quantity of tin oxide in such enamel the thinner may it be applied, whilst still retaining its covering power completely.

Enamel masses may also be prepared without any tin oxide at all, sodium antimoniate being then generally employed. However, the enamels resulting from the fusion of this latter substance with lead glass have but an ugly appearance, wherefore the sodium antimoniate is fused along with crystal glass alone. A mass yielding a very handsome enamel is composed of a mixture of 3 parts of glass, 1 part of sodium antimoniate, and a small quantity of saltpetre.

Care is necessary in preparing all these enamels that, in fusing, sufficient regard is had to the prevention of the action of any reducing agent, by employing properly fitting lids

on the crucibles. Should the fire gases penetrate into the latter the enamel mass will always be of low quality.

Composition for Coloured Enamels.

The following formula may be employed for the ground of coloured enamels :—

Sand	-	-	-	-	-	-	-	3
Chalk	-	-	-	-	-	-	-	1
Calcined borax	-	-	-	-	-	-	-	3

especially for light red, purple red, and blue, as well as for other delicate colours, since it exerts no injurious influence on the substances contained in the colours.

Another composition, fairly refractory in itself, but equally suitable for use with any colour, is given below :—

Quartz flour	-	-	-	-	-	-	-	60
Alum	-	-	-	-	-	-	-	30
Common salt	-	-	-	-	-	-	-	35
Minium	-	-	-	-	-	-	-	100
Magnesia	-	-	-	-	-	-	-	5

Coloured Translucent Enamels.

For artistic purposes (enamel painting) certain colours are required, which for the production of certain tones must be translucent. We subjoin a few prescriptions of Deck's (the Technical Director of the Sèvres Works) for the preparation of these :—

<i>Flux or Ground Mass :</i>						Soft.	Hard.
Quartz	-	-	-	-	-	4·5	5·0
Potash	-	-	-	-	-	1·5	1·5
Soda	-	-	-	-	-	7·0	7·0
Minium	-	-	-	-	-	3·5	3·0

<i>Yellow Colours :</i>		Ochre.	Ivory.	Opaque.
Soft ground mass	-	9	26	9
Quartz	-	4	10	4
Minium	-	5	13	5
Yellow ferric oxide	-	2	1·5	0·8
Antimony oxide	-	—	—	0·8

<i>Green Colours :</i>						I.	II.
Sand	-	-	-	-	-	3.5	3.0
Minium	-	-	-	-	-	5.5	5.5
Borax	-	-	-	-	-	0.5	0.5
Potash	-	-	-	-	-	0.5	1.0
Cupric oxide	-	-	-	-	-	0.4	0.4
						Camelia Green.	Olive Green.
Soft flux	-	-	-	-	9		90.0
Cupric oxide	-	-	-	-	1		3.4
Yellow ferric oxide	-	-	-	-	1		6.0
Sand	-	-	-	-	4		—
Minium	-	-	-	-	5		—
Manganese oxide	-	-	-	-	—		2.5
						Lapis Blue.	Turquoise Blue.
Flux	-	-	-	-	50.0		93.0
Cobalt oxide	-	-	-	-	0.5		—
Cupric oxide	-	-	-	-	2.5		7.0
						Garnet Red.	Violet.
Flux	-	-	-	-	41.0		50.0
Antimony oxide	-	-	-	-	1.0		—
Manganese oxide	-	-	-	-	3.0		0.5
Saltpetre	-	-	-	-	2.5		—
Soda	-	-	-	-	2.5		—
Cobalt oxide	-	-	-	-	—		0.3

According to the specification of W. B. Fitch of Deptford (German Patent 26,693), enamel decorations may be applied to glass ware by passing the glass—ornamented with letters or designs—on its way to the annealing furnace under a revolving roller of incombustible material coated with hot enamel mass; the raised portions of the glass take up the enamel, which is fired in the annealing oven. The roller is covered with asbestos, and is charged with enamel by being passed over a flat plate covered with the fused mass.

In the Japanese Village at the London Exhibition of 1885 the process followed for producing cloisonné enamel on porcelain was by bending metallic threads to match the design and then fastening them on to the unglazed or finished porcelain with a quick-drying cement. The enamel

flux was then dusted over the piece or else applied by the brush, and fused in a muffle. The whole secret of the process—apart from the skill of the workmen—rests in the composition of the enamel flux: this should not fuse to a liquid, or the fine wires would be driven out of place and the design spoiled. The flux must therefore only adhere and cement, and it consequently does not appear vitreous, but, on the contrary, granular and dull, *i.e.*, without lustre. The cementing flux must also be refractory, since it has to stand repeated exposure in the enamel kiln and remain quite hard and unchanged therein. The coloured, readily-fusible glass fluxes are pounded small—not ground fine,—stirred up with water and laid in the different enclosures. In the muffle the enamel fuses and shrinks so that the cells do not appear full, and they therefore have to be filled up and fused again some three to six times over. When after the last firing the glass flux in all the divisions, of whatever size, has a convex surface, then the final task—grinding and polishing—is performed.

The enamellers in the Japanese Exhibition at Berlin, engaged in making cloisonné enamel on copper, applied to one part of the plate the root sap of a kind of orchid. The wire used in forming the divisions is as thin as paper, about one millimetre in width, and is wound on bamboo bobbins. The enameller nips off a piece of wire with the pincers and with unexampled dexterity forms it into a heart, or the like, about as large as a pea. This cell he lays, by means of the same instrument, on to the painted part of the plate, to which it immediately adheres. In the same manner he joins cell to cell until finally a flying bird, etc., is produced. If the sticky sap has dried up, more is applied with the brush, and the laying on of the cells proceeds. Finally, the entire surface is covered and ready for soldering, for which purpose the plate is coated with a layer of powdered solder and fired

in a muffle. In a short time all the pieces of wire are soldered fast on to the plate and the actual operation of enamelling—applying and fusing the glass flux in the cells—is performed.¹

¹ *Sprechsaal*, 1885, p. 275.

CHAPTER IX.

METALLIC ORNAMENTATION.

IN addition to the coloured decorations applied to porcelain, stoneware, faience and glass, metallic ornamentations ("decoration") are also employed. For this purpose the metals are, of course, suitable in the highest degree, acting partly by reason of their characteristic colours and lustre, or else on account of the brilliant lustre they impart to surfaces, to which they are applied in thin layers in the state of fine powder.

The metals may be employed in such a manner that firing merely causes their adherence to the surface, their peculiar metallic lustre being only developed by the operation of burnishing; or they may be made to appear lustrous in the firing. In the former case the preparations are entitled "metals"; in the latter instance "lustre".

Porcelain Gilding.

In this operation both the above-named methods are employed, one of them yielding, in the first place, a dull gilding which has to be afterwards burnished, and the other producing a lustrous gilding at once, no burnishing being then required.

To gild by the first method, the finely-powdered gold is mixed with $\frac{1}{20}$ to $\frac{1}{15}$ of bismuth flux and incorporated with thick oil and oil of turpentine, then applied, fired and burnished with agate and hæmatite.

Particulars of the preparation of fine gold powder by various methods are given on p. 74 *et seq.*

The other process of gilding—the so-called “lustre” gilding of the porcelain painter—was discovered at the Meissen Porcelain Works and kept as a profound secret. This method is much cheaper than the foregoing, the expense of burnishing being saved and the layer of gold very thin, but for this reason it is less durable and should therefore not be used for articles exposed to much wear. Nevertheless, it is now very generally employed, and the durability of the gold can be increased by repeated coatings and firings.

Another gold lustre requiring no burnishing is prepared from gold fulminate, which is produced by dissolving gold in aqua regia and precipitating with sal ammoniac. The gold fulminate, which, when dry, forms a powerful detonator, must therefore be used in a moist condition. According to Dumas, it is composed of—

Gold	-	-	-	-	-	73.0 per cent.
Nitrogen	-	-	-	-	-	5.0 „
Chlorine	-	-	-	-	-	4.5 „
Ammonia	-	-	-	-	-	6.0 „
Water	-	-	-	-	-	11.5 „
						100

To apply this preparation it is ground with oil of turpentine whilst in a moist state, then applied on the glaze by a brush and without flux, and fired in the muffle. This lustre adheres fairly well, and when rubbed over with a polishing cloth acquires a brilliant gold lustre.

Dutertre's method of lustre gilding has been already described on p. 77. The following observations are directed to facilitating the preparation of gold lustre by this process: The butter of antimony referred to (the trichloride of this metal) is prepared by dissolving the natural sulphide of

antimony in hydrochloric acid and evaporating the excess of acid and water in a retort, whereupon a buttery residue is left behind. At a higher temperature the antimony trichloride distils over and is collected in a receiver. The further details of the Dutertre process are given in the proper place. When the supernatant fatty liquid has been poured off from the crystalline sediment deposited after long standing, the resulting mass, impregnated with gold, appears as a sticky liquid of a faint greenish colour. The Venice turpentine imparts to the liquid the drying property essential for the quick drying of the decorations.

The part played by the sulphur in the production of this gold lustre is not yet elucidated, only the fact being known that without it the union of the gold with the ethereal oil solution of resin is unattainable. The gold resins decompose at a moderate heat, without fusion, leaving the gold (mixed with carbon) on the surface of the object in thin laminæ. The good results of this method of gilding are based mainly on the non-fusibility of the resinous auriferous material. The gilding produced by this mixture is brilliant, but much less permanent than that prepared from gold paint by firing. The chief considerations which have led to its rapidly extended application are the very small amount of gold required to cover a given surface and the absence of the necessity of burnishing.

Carré's¹ method of lustre gilding is somewhat different from that of Dutertre: 10 grams of gold are dissolved in 100 grams of aqua regia; diluted with 150 grams of water, and shaken up with 100 grams of rectified ether, which absorbs all the gold, the ethereal solution of gold being then separated from the water by decantation. On the other hand, a solution—filtered through powdered glass, if necessary—of 20 grams of potassium sulphate in 1 litre of water is decom-

¹ Patented in England and France.

posed by 200 grams of nitric acid and the resulting precipitate of sulphur washed and re-dissolved by warming in 5 grams of nut oil mixed with 25 grams of oil of turpentine. To this solution 25 grams of oil of lavender are added, the whole being thereupon mixed with the ethereal solution of gold, evaporated to a syrup in a porcelain basin on the water bath, and mixed with 1·5 grams of bismuth oxide and 1·5 grams of lead borate. For use the mixture is diluted with a mixture of equal proportions of oil of turpentine and oil of lavender.

Other gilding compositions used, particularly for small trinkets, are partly obtainable by purchase, partly kept secret by their inventors. The Swedish chemist Gentele analysed two of these preparations, and an extract from his researches is now given.

One of the preparations, a dark red-brown liquid, obtained from Berlin, gives a very handsome and lustrous gilding. Gentele tried to produce an imitation, but was unsuccessful; the composition contained a deal of chlorine, which is a great evil, since when fired in the muffle it would destroy any colours present, and is therefore only suitable for unpainted porcelain.

Another preparation consists of a solution of gold fulminate in sulphur balsam. Black gold sulphide can also be employed instead of the fulminate, in which case a larger amount of sulphur balsam is necessary to effect solution. The painted objects are left, before firing, until the initial greenish colour has become dark: the lighter the firing the greater the lustre of the gold, but the less strongly adherent does it become. When strong firing is practised the lustre must be brought out by rubbing, when necessary, with washed chalk or magnesia.

Very common gold lustre—Burgos, or Staffordshire lustre—through which the underlying white and colours of the porcelain appear to show, is prepared by adding tin to a

solution of gold in aqua regia, and agitating the whole with sulphur balsam. A thick magma results, which parts with a large proportion of its water after standing a while, and is then suitable for use.

The gilding of fine stoneware, faience, etc., is analogous to that of porcelain.

At the Ilmenau Porcelain Works the method pursued (German Patent 36,001) for the production of dead gold or dull lustre on porcelain, stoneware, etc., is to first coat the glazed surface, to be painted, with a metallic colour consisting of minium, borax, quartz, and a colouring metallic oxide, the whole mixed up with dammar lac. When this covering is dry the design is drawn on it with coloured oil of cloves. After a few minutes the oil is wiped off, whereby the underlying dull colour is also removed, and the piece is fired. The next step is to dip the piece in, or cover the decorated surface with, very dilute hydrofluoric acid (1 litre of water to 3.75 grams of strong acid), which etches away the dull colour. The surface to be decorated is then covered with gold or lustre and this covering fired in a muffle, the gold thereafter showing up dead on the places where the dull colour has been etched, but lustrous everywhere else.

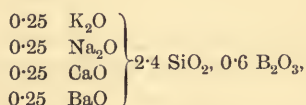
According to Teuchner-Klösterle,¹ gilding with mixed metallic gold is the oldest and most durable method. 100 parts of precipitated gold, 9.2 parts of basic nitrate of bismuth, and 9 parts of silver chloride are well moistened with water and intimately mixed by a glass runner on a glass palette. The application of strong pressure on the glass runner must be avoided, particularly towards the end of the operation, since the gold would immediately become lustrous, and so unfit for use in painting. Two or three hours are necessary for the mixture of the materials on the palette; the preparation will then—assuming the room temperature to be normal—

¹ *Sprechsaal*, 1881, p. 761.

be quite dry and fit for the painter, who applies it for decorations in the usual manner.

Burnished gold occupies an intermediate position between the old process of massive gilding and the light, cheap lustre gilding, since it gives a more solid product than the latter, and is less than half the cost of the former. It consists of 100 parts precipitated gold, 150 parts mercury oxide, 9.2 parts silver chloride and 9.2 parts basic nitrate of bismuth.

For preparing stoneware glaze coloured with gold, H. Hecht¹ employs the necessary amount of a 1 per cent. solution of gold chloride added to the syrupy glaze and maintained in a state of suspension in a large evaporating basin. The glaze is rendered alkaline by a few drops of sodium carbonate stirred in with a glass rod, and a small quantity of a solution of grape sugar is added. Moderately warmed over direct fire and kept stirred, the entire mass becomes coloured a decided red in a few minutes, and is then removed from the fire, left to cool, and afterwards washed several times. A glaze which shall have a dark red colour when fired is obtained by means of 0.1 per cent. of metallic gold per 100 grams of dry glaze. The handsomest tones are obtained from glazes free from lead : *e.g.*, 80 grams of a frit from



mixed to pulp with 20 grams of Zettlitz kaolin. A glaze containing 0.01 per cent. of metallic gold will have a delicate rose tint when fired ; one with 0.0033 per cent. of metallic gold will form yellow-rose when mixed with a little uranium glaze.

¹ *Thonindustrie Zeitung*, 1891, p. 694.

Decorating Earthenware with Noble Metals.

According to M. F. L. Ehrlich (German Patent 46,708), a fine-grained regular foundation for dull metal decoration by lustre metal can be prepared from the finely-divided alumina (Al_2O_3) obtainable by calcining aluminium compounds, especially ammonium alum. This is applied in conjunction with enamel flux to the surface of the ware, and is then fired.

Glass Gilding.

This is an operation very seldom performed ; frequently the gold is applied mechanically by covering the glass with gold leaf attached by means of copal lac.

Other methods, however, have recently come into use, whereby a finer, if not more durable, gilding is produced. In the first place there is Wernicke's process, yielding very good results, but rather cumbrous and not employed on a large scale. Dr. Böttger of Frankfurt-on-the-Main has considerably modified and simplified Wernicke's process. He prepares a solution of gold by dissolving the (acid free) chloride from 1 gram of gold in 120 c.c. of water, and a solution of 6 grams of sodium hydrate (caustic soda) in 100 c.c. of water, as well as a reducing solution by dissolving 2 grams of grape sugar in a mixture of 24 c.c. of water, 24 c.c. of 80 per cent. alcohol, and 24 c.c. of aldehyde of sp. gr. 0.870. Since this reducing liquid loses its power when stored for some time, it is therefore advisable to prepare only enough to last for a day. The gold solution must be perfectly free from other metals—especially silver—precipitable as regulus by the reducing liquid, since the gold, in presence of traces of metals, and of silver in particular, is thrown down for the most part as a powder, and the thin off-coloured coating of gold is very quickly dissolved by the glaze.

The glass objects to be gilded are placed in the gilding liquid—consisting of 1 part each of the gold and soda solutions and $\frac{1}{16}$ part of the reducing liquid—and kept there for about five minutes. If a very heavy gilding is desired the object is repeatedly dipped in the gilding liquid until the desired degree is attained.

This process is, up to the present, the safest, quickest, and most economical method known, since, provided the gold solution is free from other metals, failure is impossible, the gilding is complete within five minutes, and, finally, only a comparatively small quantity of gold adheres to the glass, the greater part remaining in the condition of loose flakes suspended in the liquid, from which it can be recovered by filtration, washing, drying, and gentle calcination, and can thereafter be used over again as fine gold for the production of gold chloride. Thoroughly permanent results are, however, not obtained by this process.

Liebig invented a materially different method, which is fairly simple and cheap, but offers no certainty in the results, the gold being occasionally—owing to some, as yet, undetermined cause—reduced in the state of powder. The use of this method on a large scale, as briefly described below, cannot be advised.

A gilding liquid is first prepared by adding to 1000 parts, by weight, of gold solution in aqua regia, 229 parts of common salt, and driving off all the free acid, by evaporation, to dryness. The residue is dissolved in water in such a manner that 100 c.c. of the liquid contain 1 gram of gold. Of this liquid 50 c.c. are mixed with 20 c.c. of soda lye (of 5°B strength—about $2\frac{1}{2}$ per cent. of caustic soda) of 1.035 sp. gr. and 300 c.c. of water in a glass flask, and concentrated by evaporation down to 250 c.c. The other moiety (50 c.c.) of the gold solution is also mixed with 20 c.c. of the same soda lye and 230 c.c. of water, and the vessel set for an hour in

boiling water. The two liquids must then be immediately united and are thereupon ready for use. It is necessary that the gilding of the various articles should be performed in quick succession, because after the expiration of 24 hours no further results can be obtained from the mixture.

To produce a gilding capable of standing hard wear and the influence of the weather, it is necessary, in this case also, to fire the finely-divided gold powder on the glass. The same procedure is adopted as for porcelain; the pulverulent, very finely-divided gold (for preparation see page 75) is mixed with a suitable flux (calcined borax), gently ground with thickened oil of turpentine or gum water, and applied with the brush on to the surface of the glass according to the design, and thereafter fired in the muffle. During the firing the organic matter volatilises or burns off, and the gold dust is cemented on to the glass surface by the melted flux. To impart lustre and the characteristic colour of gold to the fired gilding, which appears of a dull yellow-brown colour, it is first rubbed with a cloth and a little magnesia and treated with a steel burnisher, agate, or hæmatite.

J. Pratt of London (English Patent 12,014) gilds glass by first cleaning it with tin chloride and then coating with a solution of 3 parts of gold chloride, 1 part of caustic soda, dilute glycerin, and mannite.

Various Lustres.

The decoration of porcelain forms the most important branch of gilding. A description of a few other methods, less frequently employed, will now be given. Salvétat's yellow silver lustre, which is often seen on ordinary faience, will be mentioned first. This lustre presents the appearance of a lustrous metallic surface with a yellow reflection, and can be easily prepared by impregnating an oily liquid with a solution of silver in nitric acid.

Cantharides lustre.—In preparing this the above-named silver lustre, which on white surfaces looks yellow, but over blue exhibits a greenish appearance, is used. It will be evident that various combinations can be produced by altering the colour of the ground, but this lustre is seldom employed, owing to its unreliability. The main difficulty in the preparation of this lustre consists in preventing the piece from cracking under the sudden increase of temperature ensuing on its exposure to the choked fire, and in the successful conduct of this operation throughout.

The *mother-of-pearl lustre* is more frequently employed. In its preparation use is made of the Dutertre method (pp. 77 and 231), modified for the purpose in view by Brianchon, who replaces gold by the oxides of iron, lead, bismuth, uranium and silver. Certain special fluxes prepared from bismuth or lead oxide are used, the bismuth flux being preferable as resisting the high temperature better. The following substances are taken :—

Crystallised bismuth nitrate (powdered)	-	10 per cent.
Colophony	- - - - -	30 „
Oil of lavender, or turpentine	- - -	75 „

The colophony is warmed in a vessel on the sand bath, and in proportion as it melts the bismuth oxide is added bit by bit, with constant stirring. The mass soon turns brown, whereupon 40 parts of the oil of lavender or turpentine are added at once, in order to secure complete solution. The vessel is now removed from the sand bath, the mass left to cool down, and the other 35 parts of oil stirred in.

The lead flux is prepared in exactly the same way, only substituting lead oxide for the bismuth oxide.

The preparation of the lustre mass varies in accordance with the use for which it is intended. A yellow (iridescent) mother-of-pearl lustre is obtained from

Powdered uranium nitrate	-	-	-	10 per cent.
Colophony	-	-	-	30 „
Oil of turpentine	-	-	-	70 „

The colophony is melted over the sand bath, as before, and the uranium oxide added, whereupon the first moiety of the oil of turpentine is mixed in, the remainder being added after the removal of the vessel from the sand bath.

Equal portions of the above preparation and bismuth flux are mixed and applied in a thin layer to the piece of earthenware, which is then fired in a muffle. This lustre may also be used on glass, but in that case equal parts of the bismuth and lead fluxes must be used, and very often butter of antimony (p. 77) as well. The same applies to the following mother-of-pearl lustres :—

Iridescent orange and Nankin yellow lustres are made from similarly-produced preparations, viz. :—

Powdered ferric nitrate	-	-	-	15 per cent.
Colophony	-	-	-	15 „
Oil of turpentine ¹	-	-	-	40 „

This mass is mixed with the flux in the proportion of one-third of the weight ; the colour after firing will vary, according to the proportion of flux, from the reddest orange to the yellowest Nankin shade. An imitation of lustre gold is prepared by mixing the two foregoing preparations :—

Uranium preparation	-	-	-	2 to 3 per cent.
Iron preparation	-	-	-	1 „

It is probable that the iridescence of these lustres is due to the action of reducing vapours in the firing and the reactions produced by them with the iron in the glaze. Salvétat, who was the first to advance this opinion, proved that these lustres could not be produced on the glazes of biscuit porcelain—which are lead glazes, free from iron—when

¹ Added in two stages, as before.

exposed to the influence of decided reducing agents ; they merely turned black, owing to the reduced lead.

Copper lustre, which is not employed in practice, resembles Burgos lustre in appearance, and consists of cuprous silicate.

Lead lustre, which is only used in South Germany for ordinary earthenware, is of fine iridescent lustre, but can only be produced on lead glazes.

All these briefly mentioned lustres are very little used since they quickly lose their lustre and beauty, become impure, and soon disappear.

Finally, mention must be made of *platinum lustre*. According to Brongniart, this is prepared by mixing a concentrated solution of platinum with oil of lavender—or any other ethereal oil—and applying the mixture very evenly, with the brush, over those parts of the glaze to which it is desired to impart the lustre of the metallic platinum ; firing is effected in the muffle. The colour of the glaze is completely hidden, and the lustre is just as brilliant and handsome as though produced by burnishing.

*Alumina lustre*¹ belongs to the colourless lustres, which, having no covering power, allow the colour of the under layer to appear, but render the latter iridescent. Fused colours thereby become glaze-like or enamelly in character, may be applied thickly, and are fired as usual.

Alumina lustre is prepared by precipitating 4·75 grams of alum (dissolved in warm water) with 300 c.c. of a solution of soda-resin soap. An alumina resin soap is produced, which, after filtration and drying on a plate of porous clay, is dissolved in oil of turpentine, and the pale yellow liquid—the finished lustre—stored in bottles. The resin soap is prepared from 300 c.c. of normal soda solution and 90·6 grams of resin (9·36 per cent. soda, 90·64 per cent. resin acid) diluted with 10 parts of water.

¹ *Sprechsaal*, 1889, p. 578.

According to the specification of the Ilmenau Porcelain Works (German Patent 29,566) the porcelain, stoneware, etc., articles to be decorated are fired and then coated with a pulp prepared from gum and porcelain body, either by free hand or by means of stencils, in such a manner that only the surfaces to be decorated are covered. Then small pieces or splinters of comminuted glazed porcelain sherds are dusted over and the piece left to dry until these fragments are held fast by the gum, whereupon the piece is fired at a strong heat. When cooled, the raised portions are coated over with lustre gold, lustre silver, or other metallic colours, which are then fired in the muffle. The portions so treated appear as biscuit or lustrous in the finished ware.

According to A. Schierholz of Plaue (German Patent 25,246), porcelain, earthenware, glass, etc., are painted with the usual enamel colours, and then, whilst the latter are still sticky, sprinkled over with water-white or coloured strewing beads, so that the surface becomes thickly covered therewith. The article is then fired in a muffle until the applied covering is fused, whereby the whole surface is caused to unite. The underlying colours assume a peculiar lustre from the rough covering of beads.

According to W. Preussler of Liegnitz (German Patent 22,091), a compressed layer of enamel may be produced on glass by applying to the surface a semi-dry, very viscid mass of dry enamel, thick oil of turpentine and dammar lac. When dried, the coating is pressed by means of a small toothed wheel or by applying pressed paper, or the like, and forcing the projections thereon into the enamel by the aid of an india-rubber roller or a brush. The enamel is then fired.

In the above manner the shape of the figure, as well as the feathers of birds, hair of animals, veins of leaves, etc., may be reproduced in slight relief.

To produce fine-lined ornamentations, resembling intassa,

on glass, the latter, according to H. Deutsch of Zweibrücken (German Patent 22,248), is coated over with lacquer, in which the ornamentation is etched with a graver, the design being then coated with thin glue, and leaf metal applied. After drying, this is first covered with a shellac spirit varnish, and then with lacquer or oil paint.

CHAPTER X.

FIRING THE COLOURS.

1. REMARKS ON FIRING.

THE firing temperature is varied according to the material—whether glass, porcelain, stoneware, etc.—and colours under treatment. The constitution of the various objects often causes serious difficulties and important peculiarities in the operation of firing the metals and colours.

We are mainly interested in considering the firing of glass painting colours, on the one hand, and of the colours for porcelain, faience, stoneware, and enamel, on the other.

Firing Colours on Glass.

In this operation the following fundamental rule must be borne in mind :—

The warming must be only gradually increased to heat, in order to give the glass time to expand by degrees throughout its entire mass, regular warming being essential. When the fusing point is attained the heat must be slowly and gradually decreased, otherwise the glass will crack in from one to eight hours after it has been removed from the kiln and is standing in the room.

Although the firing of glass colours is more difficult than that of porcelain colours, still there have of late been devised many methods of facilitating and ensuring the accuracy of the operation. One of the most important of these is the

determination of the temperature, which we shall now consider.

According to the colour employed the glass is fired one, two, or three times, *i.e.*, when after the first or second firing the necessity for a third painting appears, or, as is often the case, is determined upon from the outset. It should be mentioned—although self-evident—that after one firing (that is, at the second painting) the pigments must be mixed with a larger proportion of flux, to prevent the first applied colours from running; likewise it is advisable to perform the second firing at a somewhat lower temperature than the first, though this is not necessarily the case.

The glass plates are placed in the kiln or muffle as soon as the gypsum or bone meal therein has attained a heat barely strong enough to burn the human skin. The firing then proceeds by degrees and is maintained until the sample shows that the desired result has been effected, whereupon the fire is drawn and the muffle left alone for 36 to 48 hours to cool, and must not be opened until it feels quite cold. If the operation has been properly performed all the colours of course exhibit their proper lustre and proportion, but if the fire has been too weak the purple will not have the proper lustre and is onion-coloured, whilst the dark blues will be insufficiently fused, appearing inflated and run together. On the other hand, under excessively strong firing the pale brick red and dark iron red will be almost destroyed, the fine purple will be violet, the glass corroded at the edges, and the presence of turbidity and small bubbles will indicate incipient fusion of the whole.

The second and third firings are performed in like manner, only the fire must not be too strong, or most of the colours will suffer.

The weightiest point in connection with muffle firing is, as already mentioned, the accurate and consistent regulation

of the fire.' For the suitable determination of the temperature in the interior of the muffle three methods are practised, none of which, however, is perfectly accurate.

The most usual, but least accurate plan, is that of observing the appearance of the glass through the sight-hole of the muffle, and determining by the colour the heat to be attained for firing the colours and metals employed. Skilled operators who have had considerable experience are seldom deceived, but since this is a property peculiar to the individual and not to be acquired by every one, even by long practice, but requiring special tact, the method presents little pretensions to accuracy.

The second means, which can be employed by any semi-experienced man, is the one most used, and is that of the test glasses or test sherds. These are small pieces of glass (or earthenware) on which colours are fired in the muffle, the colours used being such as possess the property of changing their tone under different degrees of heat.

In the first firing, gold purple alone is used. The alterations undergone by this colour under too weak or too strong a fire have already been described. For the second and third firings pale and dark red ferric oxide are more suitable. The carmine prepared from gold is employed on the test sherds for porcelain; this will be again referred to later.

The third method for determining high temperatures—that of the pyrometer (Brongniart)—would be, if it could be brought to perfection, the most certain and accurate of all. Attempts have long been made to construct a pyrometer which should fulfil all requirements, and for this purpose air thermometers, metals, and even earthenware cylinders have been employed. To render a pyrometer suitable for use in the firing of colours, several conditions are necessary which have not hitherto been found combined in any one instrument. In the first place, it must be capable of ready

manipulation and must quickly indicate the temperature of that part of the kiln in which it is situated, as well as register the progress of the fire, and at the same time be constructed in such a manner that its indications can be accurately observed. To this end the pyrometer must be long enough to be inserted a good way into the furnace, which will—particularly in the case of firing porcelain strong fire colours in the lower kiln, the walls of which are alone about 60 inches thick—necessitate a length of nearly 80 inches: for ordinary muffle furnaces a length of about 40 inches will suffice.

Wedgwood's clay pyrometer, which is based on the property of clay shrinking in bulk when heated, indicates the temperature readily and conveniently, it being merely necessary to take out the small clay cylinder and measure its contraction on a specially constructed scale. Fourmy has shown, however, that this instrument does not fulfil all the necessary requirements, in that the shrinkage of the clay is not constant at a given temperature, but depends on the rate of heating. According to the nature and preparation of the clay employed and the degree of compression undergone by the mass in forming the cylinder or cube, the variations of the latter will differ at one and the same temperature side by side in the same furnace, so that occasionally a difference of 5° to 7° is apparent. By reason of this uncertainty and irregularity of recording, the Wedgwood pyrometer is now seldom used. Each degree on this instrument is taken as equivalent to $72\frac{2}{3}^{\circ}$ C., and the middle point is $598\frac{1}{3}^{\circ}$ C.

For similar reasons the platinum pyrometer, constructed by Guyton de Morveau and Daniell, is no longer employed: the zero point in this case is $13\cdot33^{\circ}$ C., and each degree corresponds to 4° C. The low rate of expansion of this metal and the consequent difficulty of reading small changes of temperature render this pyrometer unsuitable from the outset.

The air thermometers, which are best able to indicate high temperatures accurately, are, however, difficult to insert in the furnace, and are, moreover, very inconvenient to handle. Nevertheless in firing colours on glass the air thermometer is mostly used, the porcelain test sherds affording considerable assistance.

Cherry red heat is the usual temperature at which glass colours are fired. To correctly estimate the heat of the muffle—if it is desired to do so—it is merely necessary to observe the colour of the muffle accurately, allowance being in all cases made for the daylight admitted, since this factor, be the effect exercised great or small, always tends to impart a deceptive appearance to the colour of the glowing muffle.

Firing Colours on Porcelain.

In this case also the precautionary regulations given for firing glass colours must be observed. Distinction is drawn between firing in muffles (for soft and hard muffle colours, see p. 168) and in glaze kilns. The degree of heat employed ranges from 3° to 6° of the Wedgwood pyrometer.

Both glass and porcelain colours are always fired with wood fuel. Attempts have been made to employ hard coal for this purpose, but without success, this fuel always producing a penetrating smoke, forcing its way into the muffle and endangering the colours, which it spoils without exception, the loss thus occasioned being far superior to the saving in cost accruing from the lower price of this fuel.

Here, as in firing glass colours, the most important factor influencing the success of the operation is the proper regulation of the fire. At the outset the temperature must be increased very slowly, being afterwards accelerated, and towards the end raised very quickly, whereby the recognised increase in the temperature of the muffle must be taken into

consideration. A weak fire will, it is true, cause the colours to fuse, but will leave them insufficiently vitrified and with a dull appearance.

Fourmy, to whose researches we are greatly indebted in this branch, offers an explanation of this circumstance. When glass is maintained in a fused condition at a constant temperature for some time, the small particles of the substance in the soft state alter their mutual position, and, by reason of their power of aggregation, assume a crystalline structure, whereby the glass is rendered opaque, a process on which the production of the so-called Reaumur porcelain is based. A painting that has been spoiled in this manner cannot be improved by another firing at a higher tempera-

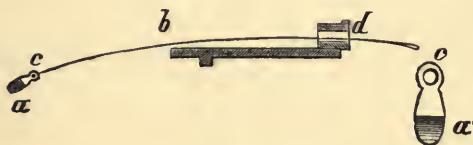


FIG. 7.

ture; on the contrary, it is made still worse, most of the colours undergoing alteration.

In the present operation also, the temperature is determined by watching the glowing ware through the hole in the muffle, and, according to the colour of the various degrees of heat observed, *viz.*, dark-red, cherry-red, whitish-red, white-red, and white—between which a skilled eye will detect a number of intermediate tones—determining the heat that must be attained for firing the different colours and metals.

Test sherds, on which the carmine colour from gold preparation is exclusively employed, are also used. The colour is applied to a small porcelain plate (*a*, Fig. 7), which is threaded on an iron wire (*b*) by means of the hole (*c*) and inserted through the aperture (*d*) of the muffle.

Brongniart drew up a scheme showing the alteration undergone by the colour at various temperatures.

1. At the temperature necessary for firing gold on soft grounds the colour is brown-red, impure brick coloured, and scarcely vitrified.

2. In the retouching fire the carmine is rose-red in the thin places, the thicker layers being somewhat brickish.

3. In the first firing of the painting the colour passes over from rose-red to purple.

4. In burning a gold ground on white glaze the rose-red has a tinge of violet.

5. When firing gold edges on plates the violet tone becomes paler and impure as the temperature rises.

6. In the fire for firing dull gold both the rose-red and the violet colorations disappear completely.

These are the chief tones assumed by the carmine: in the course of the change from one to the other there is, naturally, a number of intermediate shades.

Although carmine is a particularly suitable colour indicator, there are sundry other, apparently insignificant, circumstances which are independent of the temperature, but nevertheless exert considerable influence, *viz.*, the comparative fineness of the colour, the quantity of thickened oil employed; the manner in which the carmine is applied to the test sherds has also an appreciable influence on the results of the test. Instances are known of one and the same carmine producing at the same firing temperature very different colour tones when applied by different painters. The thickness of the colour layer (as referred to under 2, above) may also exercise great influence on the result, the thicker layers at the high temperatures employed being always somewhat inclined to be brickish, whilst the thinner layers exhibit a fine rose-red shade. Finally, the fire itself effects very different results. If, for example, it does not

burn with a clear flame, but, by reason of insufficient draught or the dampness of the wood, gives off a deal of vapour and smoke, then the rose-red colour turns to violet and is lustreless, with a greyish aureole; an irregular fire also produces certain modifications in the results.

We now come to the pyrometers, to which reference has already been made on p. 246, Brongniart's silver pyrometer being the only one now under consideration. Silver possesses

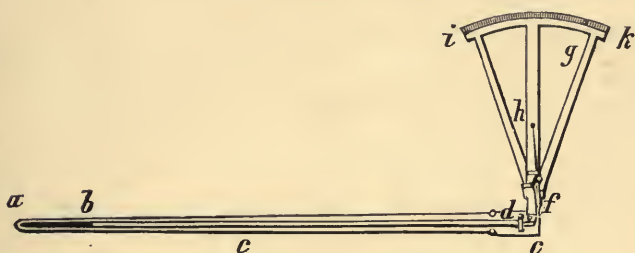


FIG. 8.

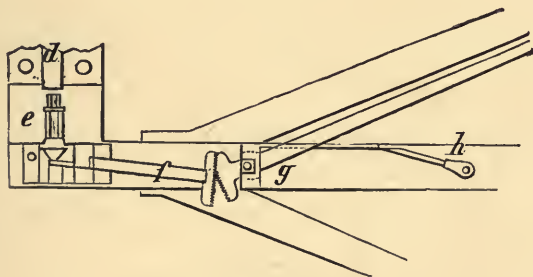


FIG. 9.

in the highest degree of all metals the properties suiting it for employment in measuring muffle temperatures, being infusible at the highest temperatures required for muffle colours. This pyrometer is depicted in Figs. 8 and 9. Here *a b* is a silver cylinder, 2 decimetres (about 8 inches) in length, which rests in the bore of a piece of porcelain biscuit (*c*), one end (*a*) of the cylinder touching the extremity of the bore.

The other end of the cylinder is in contact with a rod of porcelain biscuit (*b d*) in the same channel. In order that the expansion of the silver may be observed outside the muffle furnace, a lever (*f*) is connected to this rod by means of the copper piece (*c*), which is fitted with a screw for adjusting the length of the instrument, and moves the pointer (*g*); *h* is a steel spring for keeping the teeth of both parts in firm contact and connection with the rods *a b* and *b d*. The arc (*i k*) through which the pointer travels is divided into 300 degrees, the dimensions being calculated so that each 100 of these degrees in the arc corresponds to 2 millimetres of expansion on the part of the silver cylinder; 27—30° on the arc approximate very closely to 100° of the Centigrade thermometer. Calculated from this the fusing point of silver would be 1000° C., and as Princep has determined it to be actually 999° C., great reliance may be placed on the performance of this instrument. The firing of colours on porcelain takes place at between 200° and 250° of this pyrometer, and as silver fuses between 300° and 335° of the same scale, it is evident that the temperature required for firing the hard colours is not far removed from the fusing point of silver. Brongniart himself admitted that his pyrometer is imperfect in that it does not indicate the absolute temperature, but only the difference between the longitudinal expansion of a rod of silver 2 decimetres in length, and that of an equally long rod of porcelain biscuit. When the expansion of porcelain biscuit, which is very slight, is known, one has then only one definite figure to go upon.

The following table of comparisons drawn up by Brongniart shows the colour assumed by the carmine at different degrees of his pyrometer :—

Definition of the Fire.	Colour of the Carmine.	Degree of the Silver Pyrometer.
For firing gold on soft colour foundations	Dirty brown-red, brick-coloured, and barely vitrified	200—300°
Second retouching fire	Red, somewhat brick-coloured	250°
First retouching fire	Rose-red in thin layers, the thicker layers somewhat brickish-red	255°
For firing soft muffle colours	Purple rose-red	260°
For firing gold grounds on glaze	Rose-red with a tinge of violet	275°
For firing gold rims on plates	Violet	287°
For firing hard muffle colours	Pale violet	290°
For firing dull gold	The rose-red colour disappears completely, leaving faint traces of violet	315—320° Fusing point of silver

2. THE MUFFLE.

There are two kinds of furnaces, *viz.*, those with fixed and those with removable muffles; the latter are very rarely used in manufacturers' works, only for furnaces set up by amateurs and dilettanti. In both kinds the method of arrangement is the same. The object of the muffle itself is to protect the painted article from contact with the flame, since both the latter and the particles of ash, carbon and other injurious substances it contains exercise a highly prejudicial action

on the colours. They also serve to communicate a regular temperature to the colour, on which account they, as well as the interior part of the furnace itself, must be made of fire-clay. Muffles of cast iron, brass, etc., are also employed, but only for ordinary ware and for colours requiring merely a low firing temperature. The subjoined figure (10) shows a cast iron muffle of this class; *i* is the flue for carrying away any products of combustion given off during the firing. The muffle opens at *a a* for inserting or removing the glass, porcelain, etc.; *e e* is the door; *m m* are the sight-holes through which the test sherds are inserted and the progress of the

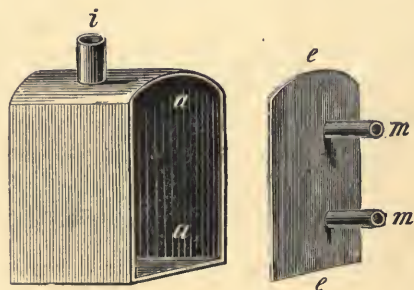


FIG. 10.

operation observed. There is but little difference between the muffles for glass and those for porcelain except that the former are of somewhat larger size.

It has already been mentioned that the materials for constructing muffles must consist of good fire-clay, free from lime, bitumen or pyrites (substances exerting an injurious action on the colours), and must be capable of resisting a fairly strong fire heat without fusing or softening. To modify the excessive plasticity of the clay, a little sand is mixed along with it, the state of division varying with the size of the muffle.

The form and dimensions of the muffles vary considerably,

according to the purpose in view. That indicated in Fig. 10 is the one in most general use, but round and square muffles, either turned or moulded, are also employed. Figs. 11 and 12 display the details of a muffle described by Brongniart and used by him at Sèvres, Fig. 11 showing the cross section and Fig. 12 the side view.

A is the muffle ; the convex top is pierced by an aperture

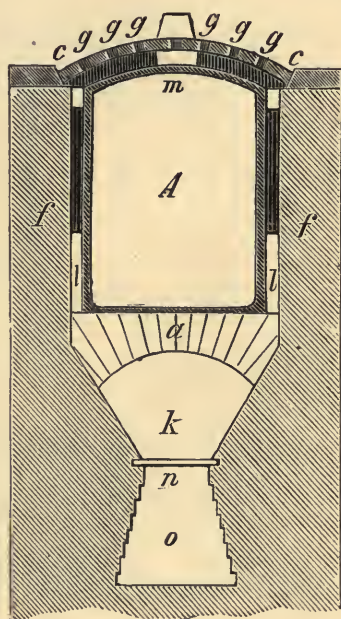


FIG. 11.

(*m*) for the escape of oil vapours and evolved gases. The sight-hole (*c*), which is seen only in Fig. 12, consists of a conical tube by means of which the progress of the firing can be observed and the test sherds introduced. This tube is fastened on to the movable front plate (*e*), which serves as a door. When the glass plate, piece of ware, or other article to be fired is inserted in the muffle, the door or front plate is fixed

in position and tightly luted with clay. The muffle rests on three arches (*a a a*) above the fireplace; the arch *c c*, a little above the muffle, contains at the same time the flue (*g*), through which the flame passes; *d f* are the walls of the furnace, of which *d* is only set in position after the articles have been placed in the muffle and the door of the latter is

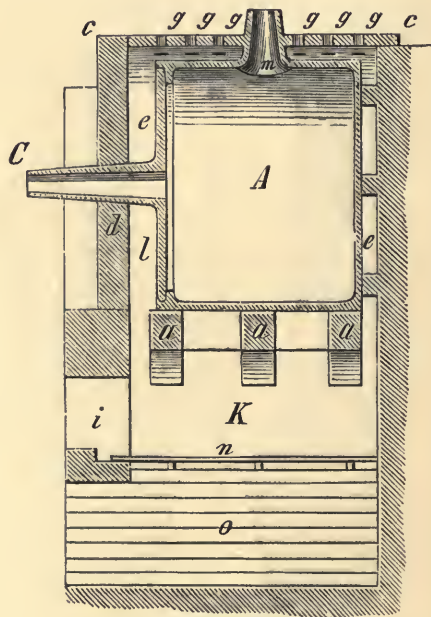


FIG. 12.

luted; *k* is the hearth, *n* the fire bars, and *o* the ash pit; the opening *i* serves for feeding the fire with fuel. The flames circulate in the space *l l* between the external walls and those of the muffle, which space should, in order to induce the necessary draught, be neither too wide nor too constricted; the most favourable width is 30 centimetres (12 inches), but considerable deviations are met with.

A front view of a muffle furnace is shown in Fig. 13, the direction of the flame being indicated by arrows and the dotted lines *d e*. Sometimes this muffle is built without a chimney, in which case the vapours escape through the test hole (*c*), but this arrangement is, for obvious reasons, not recommended. Others perforate the outer wall (*f*) with several apertures—which are, of course, closed up during the firing—in order to facilitate the rapid cooling down of the

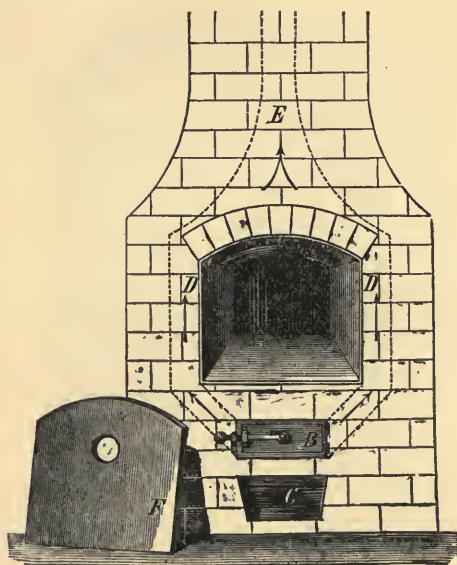


FIG. 13.

furnace. Brongniart recommends the insertion of a plate (*c*) on the side of the muffle opposite to the fire, in order to better protect the contents from dust, ash, or sparks. The fire bars should be movable, and an arrangement provided for bringing them nearer to, or farther away from, the muffle, as circumstances may render advisable.

The Meissen muffle furnaces are constructed in this manner, and several of the muffles are connected with a

common chimney, the communication with the flues of the individual muffles being shut off at will.

For paintings on glass a somewhat different form of muffle is employed at Sèvres, the height being rather greater than the width. One of these muffles is shown in Fig. 14, which also indicates the mode of inserting the various articles to be fired. *a* is a valuable painting, which is placed with the coloured side inwards, in order that it may be sheltered

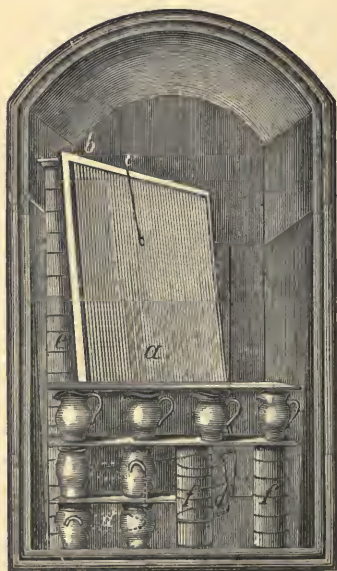


FIG. 14.

from dust, and is inclined against the plate *b*, which may be of biscuit, contact between the two plates being prevented by the interposition of a slip of biscuit (*c*) not seen in the drawing. Both plates are supported on saggers (*d d*) and rest against others (*e*); the saggers *f f* serve to support other objects filling the remainder of the muffle; they are carried right up to the plates, an arrangement not depicted in the drawing, as it would hide the chief piece from view. As

occasionally the muffle cracks during the firing and admits gas and smoke, the pieces are protected by lining the inner walls of the muffle with old damaged plates of biscuit (*g g*). The test sherd *h* (painted with carmine, see p. 246) is suspended at the centre of the painting to enable the temperature to be determined with the greatest possible accuracy.

For the construction of a kiln with a large muffle for firing large glass pictures, the subjoined details will be found

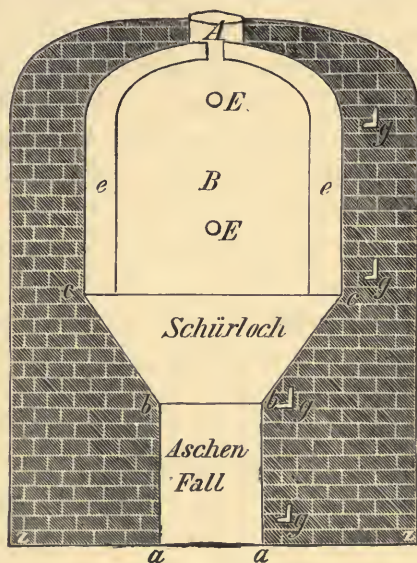


FIG. 15.

Schürloch = Hearth.

Aschenfall = Ash pit.

—as they have already proved in the author's experience and at Munich—useful. Messel describes the construction as follows :—

A domed furnace, about 3 ft. 4 ins. high and 3 ft. 9 ins. long, containing a fire grate and ash pit (Fig. 15), is built. From the bottom up to this point the brickwork is some 2 ft. in thickness on either side, and 1½ ft. high, but thence

upwards is sloped away. At the height of $1\frac{1}{2}$ ft., the space between the walls being only 1 ft. 4 ins., bars 1 in. thick are set, half an inch apart, and the opening *b b* thereby covered over. Above this grating the brickwork is continued for another $1\frac{1}{2}$ ft., the walls being sloped away on the inside until at *c c* the internal space measures 3 ft. 4 ins. across, the walls being then only 8 ins. thick.

Arrived so far, three 1 to 2 in. cast iron bars are set at intervals across the opening, and the walls are carried up for a further 2 ft. or only $1\frac{1}{2}$ ft., whereupon a sketch showing the width of the furnace is made on paper by drawing a straight line of the same length as the space between the two walls. A pair of compasses being opened out to correspond to one half of the open space or half the right line, a semicircle centred at the centre of the line is then described above it. After drawing this line a firebrick is measured across the width, the compass spread out to correspond to this increased distance and then employed to describe a second arch over the first one, the two arches indicating the dome of the furnace. It is well to measure the thickness of a firebrick and set this out on the upper arch ; by then drawing slanting lines from the centre of the base line to the points corresponding to the edges of the firebricks, the amount of decrease required in the inner edges to form the perfect arch will be ascertained. The bricks can be formed to shape by marking off the amount to be cut off, rough hewing this with a chisel or other instrument, and finishing by wet grinding on sandstone. The bricks should fit so accurately that scarcely a trowelful of fireclay will be required in the dome. When this is accomplished wooden arches must be made, like those used by builders in arching cellars, but of course smaller, and two or three of these being nailed together by boards and set up on the wall, the building is continued all round until the centre is reached. The key-

stone should not be prepared until the last moment, so that it can be ground to fit the opening exactly. Of course fire-clay,¹ and not ordinary mortar, must be used in setting this brickwork, and the firebricks, instead of ordinary earth, must be made of earth with which fine white sand and powdered firebrick, in the proportion of $\frac{1}{3}$ to $\frac{1}{2}$, are incorporated. In the centre of the furnace a round 9-inch hole (*A*) is left, over which is built a firebrick chimney 4 or 5 ft. high. The width of the chimney does not depend solely on the size of the furnace, but chiefly on the draught—which can never be accurately estimated in advance—of the apparatus and flue. For the first 3 ft. from the furnace the chimney must be of stone, because this portion is subjected to the most intense heat of the flame. Beyond the above distance strong stove pipe may be used, and should be wider at the bottom than the top in order to induce a better draught.

The brickwork furnace will now have these dimensions : *a a*, 1 ft. 4 ins. ; *a-z*, 2 ft. wall ; *a a-b b*, 1 ft. high ; *b b-c c*, $1\frac{1}{2}$ ft. long. The apertures *b b-c c* constitute the fire door for inserting the wood fuel ; *a a-b b* is the ash pit ; *c c*, on either side of *B*, is the flue (2 ins. wide) for the circulation of the flame around the cast iron, or better, fireclay, muffle, which has one or two test holes (*E E*) and a short chimney reaching into the aperture *A*, to carry off any gases, etc., volatilised in the muffle. The dimensions of the muffle are, width, 3 ft., length, 3 ft. 5 ins., so that when the door of the furnace is in position there is a space of 2 ins. for the circulation of the flame. By each of the door openings, *e.g.*, *a a-b b*, iron hooks to carry the heavy doors of iron covered thickly with clay are driven into the brickwork. These hooks are of wrought bar iron

¹This is prepared of $\frac{3}{4}$ good potters' clay, $\frac{1}{8}$ fine white sand, $\frac{1}{8}$ powdered very strongly fired pottery.

driven at least 2 ft. into the wall. The doors being extremely heavy by reason of the protecting layer of fireclay are consequently liable to draw out and fall if not kept up by strong wrought supports. Each door has in addition a smaller door in the centre, which, in the under one, serves to regulate the draught, whilst that in the upper door allows the temperature of the furnace and its contents to be observed, the test sherds to be withdrawn, and the regulation of the firing to be superintended. The muffles for these furnaces are generally arranged so that four to six plates can be inserted. A similar muffle, for glass painting only, is shown in Fig. 16 (Messel pattern), the one side being depicted as though transparent. On the inside of this muffle are fixed three pairs of parallel slides of clay or iron (depending on the material employed for the muffle), and on these slides are placed, through the open end *E*, earthenware plates, which, however, must be shorter than the muffle—*e.g.*, if the latter be 3 ft. 5 ins. long, the plates must not be longer than 3 ft. 1 in.—so that there may be space for the unrestricted circulation of the heated air by which the colours are fused. The plates (*c*) are therefore placed in the centre of the muffle, so as to leave an equal space at either end, the plates being supported at the two sides.

At each of the four corners of the plates a 1-inch cube (*d d*) is placed, and on these again a somewhat smaller plate (*c c*). In each of these three compartments there now lies on the plate a glass picture or the component parts thereof. The door plate (*B*) of this muffle is fitted with three small tubes, $1\frac{1}{2}$ ins. long, each being arranged to enable a plate to be examined. This, without being absolutely necessary, is convenient for a not thoroughly experienced operator, since he is thereby enabled to inspect all the plates during the firing. Of course the door must in this case have also three little doors, about $2-2\frac{1}{2}$ ins. in size, corresponding exactly with

the tubes ; and the tubes of the muffle must be provided with iron or clay plugs for closing.

Firing is performed in a furnace of this class by lighting a small fire, the plates being already in the muffle, which is left open until sufficiently warmed for condensation to have ceased and there are no drops of moisture left under the plates, whereupon the sheets of glass to be treated are inserted upright into the furnace by means of any contrivance which will keep them in place so that they attain the same temperature as the plates, an operation generally taking about half an hour. When the kiln, plates and glass are evenly

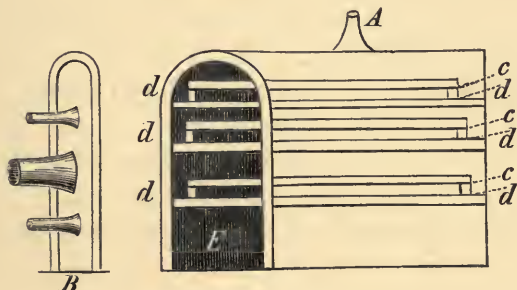


FIG. 16.

warmed to a degree whereat the hand may, without inconvenience, be pressed on the bone meal covering the plates, the latter are taken out, the upper one removed, the lower picture placed on the large plate, the upper one laid on its side and a picture laid on this also, both plates being then rested on one of the sets of slides in the muffle. The other plates are treated in precisely the same manner, and as soon as they are all in the muffle the door or front plate (*B*) is slipped into its groove from the top and the pictures shut up. The edges of the door-piece are luted with loam, but the draught hole or test hole, through which the test pieces are inserted, is left open (see Fig. 16).

When everything is thus sealed up, the kiln door is also closed and luted and the fire gradually increased.

To fire properly, a red heat, or a temperature sufficient to fuse the colours on the test sherds, must be produced, which generally takes five or six hours. At the end of the first three hours one of the little doors in the large upper door is opened and the muffle examined. If it is found that this is almost at white heat with the flame playing in blue points over the furnace, then the stopper in the test hole is removed by the tongs and a test sherd taken out. According to the colour of this (see p. 253) the firing is proceeded with, everything being quickly shut up again, or, in the most favourable event, only the opening of the muffle, and all the little doors are simply closed, the burning wood is removed, the ash pit and fire door are shut tight, and a couple of bricks placed over the top outlet pipe, in order to keep the heat in completely. Only at the end of three days, when the furnace is perfectly cold, may the pictures be removed. It should be stated that the same procedure is observed even if the colours on the test sherds have not attained their full lustre, since the heat of the muffle increases somewhat even after the external source of heat has been removed.

The top and bottom layers of paintings are always exposed to the greatest heat, and it has therefore to be arranged when firing in this way that the plates fired for the first time are placed on the top; those undergoing a second firing, at the bottom; and those fired for the last time, in the middle row.

The case frequently arises where one is not in a position to fire such large furnaces for glass paintings or where the space at disposal is insufficient. In such instances (the circumstances of dilettanti being chiefly considered) the following plan, given by Geffert, will be found suitable:—

Any ordinary stove can be made to serve as a perfectly

utilisable furnace, and every simple hearth is capable of adaptation into a suitable furnace by the aid of a few fire-bricks, tiles and iron rods. The other necessary apparatus consist of a muffle, an iron coal-shovel, an iron fire-tongs, a tongs for drawing the test samples, and a tub for quenching the coals.

When a cast iron or graphite muffle is not at disposal, one can easily be prepared of calcined pottery, the size varying according to requirements. To be more refractory, the materials should consist of a mixture of 2 parts of clay and 1 of fine sand. The shape of the muffle is a long quadrilateral, 12 ins. long at the outside, 10 ins. wide, and 5 ins. high, and must be, of course, large enough to contain the largest piece that will have to be fired, without the edges of the latter coming in contact with the sides of the muffle. In the middle of one of the short sides there is an aperture, 5 ins. long and 3 lines wide, for drawing the test samples, and the muffle is closed by a lid of proper size pierced with two round holes, $1\frac{1}{2}$ ins. in diameter, opening on the outside into tubes $2\frac{1}{2}$ ins. in length.

A square furnace is next built, the internal dimensions of which exceed the size of the muffle by 4 ins. in length and breadth. This is made solely of firebricks laid one upon another so that on the side next the operator there is left a hole, 3 ins. high from the ground up and 1 ft. wide, for regulating the subsequent firing. When the structure has attained a height of 4 ins. on all sides, a horizontal grating is formed by two iron rods set on the long sides of brickwork. On this the muffle is placed so that the test hole is turned towards the operator, and the glass being laid in the muffle, the walls of the furnace are built up higher until they over-top by an inch the pipe ($2\frac{1}{2}$ ins. long) in the muffle roof, a hole being left in the front wall, $3\frac{1}{2} \times 3$ ins., to correspond with the test hole in the muffle. Both the apertures in the

front wall of the furnace must be provided with covers, the lower one (fire door) consisting of an iron plate covered with clay, and the upper one (corresponding to the test hole of the muffle) with a stone. Each cover must fit exactly and be the same thickness as the walls.

The painted glass to be fired is inserted as follows: Well burned lime is sprinkled over with a little water and, when it falls apart, dried thoroughly over the fire. This powder is sifted through a coarse hair sieve on to the bottom of the muffle to the depth of an inch, then carefully levelled (otherwise the glass plates would warp in the firing) and the glass plates placed thereon in such a manner that they touch neither the sides nor the floor of the muffle. Then another thin layer of lime is spread over the glass and a second set of glasses laid on this again, the operation being repeated until the centre of the muffle and the opening for removing the test samples are reached, whereupon a sample glass (6 or 7 ins. long by 1 in. wide), painted with the colours to be fired, is laid on the surface, also resting on, and being covered over with, lime. One end of the sample glass reaches to the centre of the muffle, the other projecting about half an inch out of the test hole, to facilitate its removal by the tongs. The muffle is then filled up to the top with successive layers of glass and lime as before. If only one piece of coloured glass is to be fired, plain glass is employed for filling the muffle (along with lime), and the piece to be fired is placed in one of the central layers and the muffle covered up.

In each of the tubes in the cover a strip of test glass, 5 to 6 ins. in length and 1 in. wide, is inserted vertically and in such a manner that the lower end stands in the uppermost stratum of lime in the muffle, the upper part projecting about 2 ins. out of the tubes. Then after the openings in the front wall have been closed by their stoppers, firing is begun by placing some glowing coals on the hearth and fill-

ing all the spaces between the walls of the furnace and the muffle with wood charcoal—some of it already glowing—up to and above the top of the muffle, but allowing the test samples to project; the fuel will then quickly become thoroughly ignited. Some iron rods are then laid across the top of the walls, and over these are set pieces of roofing slate to cover the furnace all over, with the exception of a hole about a foot in diameter which is left in the centre.

It should be here remarked that, for ensuring the greater success of the operation, new muffles, or those that have been out of use for some time, should first be heated to redness empty, by proceeding in the above-described manner, just as if they contained a charge of glass. Heating should be continued until white heat is attained and the muffles left to cool by themselves in the furnace after the fire is drawn. Only when thoroughly cooled down can they be relied on for use.

In the subsequent firing of the charge care must be taken that the heat is applied evenly on all sides, and the strength of the fire must be kept up by continual additions of charcoal. When the muffle exhibits a dark red glow, and the test samples bend and the colours thereon—when the strips have been taken out and laid to cool gradually on the cover of the furnace—are properly fused, and have a fine appearance, all of which should result at the sixth or seventh hour of firing, then the fire is drawn as quickly as possible, but carefully, so as to avoid shaking the muffle; and all the openings, including that in the top, stopped and luted, the furnace being left to cool down very slowly, an operation that will be completed in twenty-four to thirty-six hours.

The fuel is quenched in a tub of water in order that it may be used over again.

When the cooling down is accomplished, the glasses are taken out of the muffle, cleaned with brushes and lukewarm

water, and carefully dried. In the second firing the heat must not be so intense as at the first operation.

A short description of the different forms of muffles and furnaces still remains to be given. The English muffle furnaces for firing fine stoneware come first under consideration. These muffle furnaces are the largest employed anywhere, and, as it is impossible to construct them in one piece, they are made of small rectangular plates, in which rabbets are cut half way through the thickness of the plate. Muffles made in this way present the advantage over all other systems of not easily cracking or forming fissures through which the smoke can penetrate and injure the contents. This also explains why hard coal is used for fuel in the English furnaces, whereas on the Continent wood is exclusively employed. In order to economise fuel, material, etc., it is customary to set several muffles in a large four-sided kiln. Each muffle has at least three fireplaces set in the walls of the kiln and completely separated from the muffle chamber, so that no ash, dust, etc., can penetrate into the muffles and spoil the paintings. A chief point of difference between the arrangement of the English and the French and German muffle systems consists in the former having no heating flue on the front side next the hearth, an arrangement justified by the circumstance that this front part by being nearest the fire receives enough heat without. The Meissen muffle furnaces are similar to the Sèvres system, but have the fire door on the side opposite the entrance door, and the grating, instead of iron bars, is made of fireclay tiles, set edgewise, to form a grid. In all other particulars they are identical with the French furnaces.

There now remains only the description of the Viennese and Berlin muffles, both of which forms are almost entirely discarded. These were built with back-flame fires situated on the longer side of the muffle, and, as a rule, the door-

plate of the Berlin muffles was simply placed in position without being luted, the gases, etc., from the muffle escaping through the apertures in this plate, since no special outlet was provided. The Viennese muffles were never much good in practice, being set up in pairs in one furnace, whereby, although a saving in materials and fuel was effected, almost insuperable difficulties in the way of maintaining an

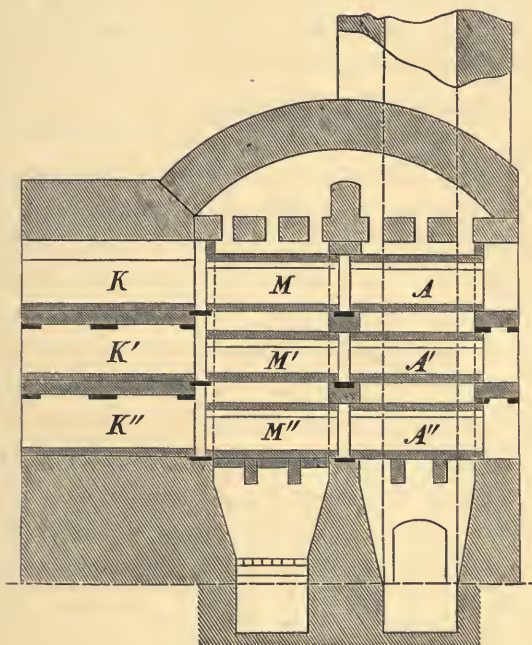


FIG. 17.

even temperature in the two muffles arose. The Sèvres muffles and furnaces, which behave in a very satisfactory manner, are mostly in use at the present time, and are worthy of high commendation.

Draught Muffles for Porcelain Paintings.—According to O. Sembach (*Sprechsaal*, 1892, p. 385), the muffles for preliminary warming are heated by the returned fire. The cold

filled pans are (Fig. 17) inserted in *A* and *A'*, where they are warmed, whilst the pans in *M M'* are receiving the necessary fusing heat. When that is accomplished the damper *S'*, between the muffle and the cooling chamber, is drawn, the door of the latter is opened and a long hook introduced, by means of which the pan is drawn out of the muffle *M* into the cooling pipe *K*, whereupon the door of the latter and the damper *S'* are immediately closed again, thus shutting off the muffle from the second cooling chamber completely. The damper *S'*, between the muffle *M* and the warmer *A*, is then drawn, and after the door plate on the exterior side of *A* has been removed the warmed pan is pushed, by means of the same hook or crook-shaped instrument, from *A* into *M*, the damper *S'* being thereupon closed and a fresh filled pan placed in *A*, which may be done by hand, though tools, such as tongs or forks, must be used for drawing the cooled pans out of *K*. When the work has been going on for some time, and the cooling chambers have thereby attained a high temperature, the erection of a second set of coolers, as close to the furnace as possible, is necessary for many kinds of porcelain and other articles.

In filling the muffle with porcelain ware for firing, as many pieces as there is room for should be inserted, the form of the objects, and the tenderness and amount of the colours, having also to be taken into consideration. Ware with simple gold decorations can be crowded as close as the pieces can be got together, whereas painted articles must stand somewhat further apart, in order that the volatile substances employed in grinding the colours may have space to vaporise without their fumes attacking and reducing the colours of the other objects in their vicinity.

The following remarks apply for the most part to earthenware, *i.e.*, porcelain, stoneware, faience, etc., only, the firing of glass paintings having already been exhaustively described

in the present section. Nevertheless, a number of the practical hints here given will be also of value in the latter operation.

An axiom, derived from experience, and applying to all kinds of colours, is that an old muffle always produces better firing than new ones ; in fact, it is very seldom that the first charge in a new muffle is fired clean. The muffle should therefore be cleaned by one or two heatings, and it is well to apply a coating of minium, particularly if the muffle is hard to purify. Many recommend the replacing of minium by borax as a coating for the inner walls of the muffle, since the capacity of the latter for conducting heat is said to be thereby diminished, the glazed walls reflecting the radiant heat, and thus exercising considerable influence on the better firing and vitrification of the colours. In practice, however, this method has extended but little.

After a muffle has been in use for some time cracks are frequently formed, which may be repaired by binding with iron (or better still, but more expensively, platinum ¹) wire and cementing with clay ; the muffle may be used so long as it is in a condition to keep out smoke. In order to obviate this continual cracking of the muffles attempts have been made to construct them of cast iron and of strong sheet iron, but without finding a really efficient substitute, the iron cracking just as easily under a slight shock or rapid change of temperature. Such muffles are never employed for large or valuable objects.

Before inserting the painted articles the muffle must be heated to a certain degree, and the same temperature must be maintained whilst the articles are being placed in position. The pieces must also have been thoroughly dried and suitably warmed in a special drying oven near the muffle. Without these precautions the moisture in the cold muffle would be

¹ This is less subject to change, and expands but very slightly indeed.

deposited on the painted articles and cover them with a coating of liquid which would be in many respects injurious to the colours. The temperature of the muffles and drying ovens should attain 100° C. (that of boiling water), which will have great influence on the beauty of the colours, and should on no account be neglected.

Enamel is fired in muffles that are only imperfectly closed, so that a certain amount of air may circulate through them, a better effect being thereby obtained than if the muffles are shut up tight. This method has also been employed with advantage in the case of small pieces, but for large articles the well-founded dread of the ware cracking militates against its adoption.

The door or door plate of the muffle must be very carefully luted, especially at the bottom, to prevent the irruption of any ash or smoke during the firing. Such particular care is not necessary in the upper portion, since the strong draught induced through the test hole and the aperture in the dome of the muffle prevents these impurities from penetrating.

It has been already mentioned that wood forms the chief fuel for muffle furnaces. Sound, dry wood in blocks 8 to 12 ins. in diameter will give a very strong and clear fire if burned in a suitably constructed furnace, and will fire the most difficult and expensive paintings in the most satisfactory manner. The opinion was held for a long time that if wood charcoal were employed for firing the colours greater purity would result, but the use of this fuel has gradually declined, the constant piling up and pressing down required being not only tiring to the operator, but also producing a penetrating dust, and because a greater number of the dreaded cracks were caused in the muffles. Care must be taken in wood firing to have a long and strong flame; poplar, birch and pine are the most suitable, and are greatly

to be preferred to the hard woods. The wood employed must be perfectly dry and cut in lengths suitable to the size of the furnace.

In warming up the large muffles thick blocks are used, the thinner ones being employed to accelerate the attainment of the necessary temperature. When the stage is reached at which it is desired to test the temperature logs of medium thickness are taken, to prevent in some measure the so-called "after-burning," a phenomenon accounted for by Brongniart by the explanation that, when a fuel, such as wood charcoal, which gives out a great amount of heat suddenly, is employed, or when the firing is pushed on too rapidly, the temperature in the interior of the muffle continues to increase although the fire-box or hearth has been cleared of all glowing fuel and the muffle no longer receives heat from the outside. Occasionally, the internal temperature will rise some 15° of the silver pyrometer in a quarter of an hour—a phenomenon attributable to the gradual delivery of heat internally by the muffle (notwithstanding the cessation of the external supply), whereby the interior temperature rises.

With the exception of Wedgwood porcelain, hard coals are seldom employed for firing colours on glass or porcelain.

It is necessary to be acquainted with the distribution of heat inside the muffle in order to place the various pieces in situations where they will be exposed to the temperatures requisite for firing their colours. Partition walls tend to make the distribution of the heat irregular, and should therefore be, as far as possible, discarded. Flat pieces of ware, such as plates and dishes, are usually laid horizontally and with the coloured side downwards. Some porcelain painters, however, claim to have found that when the colours are in this manner brought into contact with the ascending heat currents they frequently undergo alteration and vitrify badly.

Of course the pieces must be so placed in the muffle that they are protected as far as possible on the coloured side from contact with smoke, dust, etc. Salvétat utters a note of warning against the employment of supports made of burned earth or porcelain biscuit, these substances, by reason of their absorptive character, easily taking up the flux and, by retarding vitrification, causing a considerable amount of damage.

CHAPTER XI.

ACCIDENTS OCCASIONALLY SUPERVENING DURING THE PROCESS OF FIRING.

THE most critical stage in painting on glass or porcelain is encountered in the firing process, since a variety of factors capable of partially or completely destroying the colours then come into operation. Defects or imperfections in the painting are most easily caused by wrong methods of regulating the fire ; too strong a fire causing the colours to lose their strength and to mix, whereby sundry interactions occur, and the colours least attacked—blue, green and black—are left predominant, whilst rose-red and grey colours change their shade and disappear completely. Red passes into dark brown, and brown is converted into black. If the fire has been kept too strong for some time there is no remedy, but if the decomposition of the colours remains incomplete an attempt may at least be made to remove and replace the colours most affected, whereby a fresh firing will have to be performed. It is, however, as a rule, impossible to restore the painting by this means when the fire has been so excessively strong that all the colours have become more or less affected, or when the evil is occasioned in the course of the second or, still worse, the third firing.

If, on the other hand, the pieces have been exposed to too slack a fire, the colours remain dull, and the gold will not last ; the matter-of-course suggestion that this can be remedied by a second firing is, however, seldom found to be reliable in practice, and never in the case of colours that

have become hardened, the only action of the more intense fire necessary being to alter the more susceptible colours without properly vitrifying those that are harder. This defect is more easily remedied by applying another coating of the same colour and carefully firing again. These tasks are the most difficult of all that have to be performed, and can only be satisfactorily attempted by careful and experienced operators.

Very frequently bad and defective results are obtained even when the fire has been properly regulated. The blame is then attachable to a lack of skill or care on the part of the painter with regard to the mixture of the colours and the selection of the oil employed for grinding same.

Cracking or flaking off is one of the most disagreeable defects that can occur, and is caused either by the colours having been laid on too thick or badly mixed, or by the employment of too high a temperature in firing.

If the flaking off is due to the colours themselves, the remaining portion still adherent to the ware may be removed by rubbing over with fine clayey sandstone (green sandstone). This is, however, a task of great difficulty when the operation has to be confined to the exact limits of the colour to be removed; moreover, the glaze is roughened, and will impart this roughness to the fresh colour. The work may be facilitated and accelerated by means of hydrofluoric acid,¹ although this substance should only be used with the greatest care, owing to its powerful corrosive and destructive properties. If a few colours are to be removed from a painting, etc., it is merely necessary to pass over the surface a brush dipped in hydrofluoric acid, whereupon the acid will dissolve and wipe out the colours just as pencil marks are removed by india-rubber. As soon as the colours have vanished the surface must be washed, frequently and with a copious supply

¹ Hydrofluoric acid must be kept in leaden or guttapercha bottles.

of water, and cleansed to remove every trace of the acid, which would inevitably destroy all the other colours in the muffle during firing.

As has already been mentioned, should the flaking of the colour be due to excessive firing, the removal of the affected surface by rubbing or etching is not only impracticable but also leads to much greater evils, since the re-firing will affect the adjoining surfaces and induce these also to splinter off.

Another very unwelcome fault which occasionally results from the firing is the dulness exhibited by some colours even in the neighbourhood of others with a beautiful lustre. This defect is often called the "damping" of the colour, and can only be explained by the assumption that an unsuitable addition of a hard colour has been made with the principal colour in order to produce a modification in tone. It may be easily rectified by the application of a thin layer of readily fusible colour and then firing again, either once or several times. Success mostly ensues at the second or third attempt, but should this not occur, the only course remaining is to polish the dull surface by rubbing, so as to remove, in part at least, the unfavourable impression created by a dull surface in the midst of lustrous colours.

Many attempts have been made to find a suitable material for polishing, and various materials, such as tripoli, emery, punice, etc., have been tried, but without success, some being too soft and others too hard. The best results are obtained from finely powdered glaze, since this has the right degree of hardness and produces the desired effect without giving rise to streakiness or removing the colour, except, of course, such colours as are laid on so thin and are so soft that they will not stand rubbing at all. Polishing with glass powder is effected by the aid of a stick of soft wood, the rubbing part of which is cut to the desired form.

Azure blue is frequently found to be lustreless after the second firing, the blue then assuming a gritty appearance. This defect can only be remedied by applying a fresh coating of the same blue.

Another fault is the contraction or aggregation of the particles of colour (already mentioned on p. 169). In such cases the colour balls in small particles, thus giving rise to the formation of a number of vacant white patches, which appear almost as if the colour had flaked off, although it can easily be discerned that the colour has drawn together into small projecting fused heaps. The sole cause of this is to be found in the oil, used for grinding the colours, having become too strongly thickened and resinified by the action of the air. This will never occur with doubly refined oil. From the foregoing it will also be evident that this defect arises more frequently in summer than in winter.

The appearance of black specks is also a defect which becomes manifest, sometimes to greater, sometimes to smaller extent, and the formation of which is due to reduction of the lead oxide. This defect most frequently attaches to sky-blue and grey colours, both on porcelain and on enamel or faience. Sometimes, but not always, the specks disappear in the second firing; in the latter event the piece is totally spoiled.

The above constitute the chief accidents and happenings encountered in firing colours. It now only remains to make a few observations—(a) on the influence of the body and glaze on the colours, and (b) on the influence exerted by the vapours evolved during the operation.

The influence of the glaze and the body—according as they contain boracic acid, silica, and the oxides of lime, sodium, and lead—is very great, and exerts an important action on the shading of the colours after firing; this action is of a nature partly chemical and partly physical.

In the first connection the lead oxide, essentially necessary for the preparation of certain colours, has a decidedly injurious effect on the development of other colours, especially the gold colours, which are thereby rendered impure, lustreless, and of a violet shade, because the fluxes used for fusing these colours already contain a sufficient amount of lead oxide. Kaolin also sometimes acts unfavourably on gold colours, especially on carmine, so that it is occasionally found impossible to maintain their pristine tone.

Equally injurious is the effect of an excess of alkali; though potash and soda are necessary for the attainment of beauty in the colours, yet, on the other hand, they give rise to the occurrence of many drawbacks when they predominate in the glaze, their chief activity being displayed towards chromic oxide, which they convert into a yellow chromate. When, therefore, chrome green colours are fired on an underlying surface containing too much alkali, the colours are decomposed and turn yellow, the action extending also to the adjacent colours; boracic acid glazes never give rise to this defect.

A noteworthy effect is produced by tin oxide, which is frequently mixed with the glazes to render them opaque. When one of these tin oxide glazes commences to fuse in the firing, the colours thereon are altered, assume a certain degree of opacity, and, in consequence of the presence of tin oxide, will no longer mix.

These defects and injuries to the painting occur much more rarely and are much less to be dreaded if the firing be conducted at such a temperature that the glazes are neither fused nor softened.

The physical influence referred to as exercised by the body brings greater evils in its train, and such as are seldom capable of remedy. These defects, resulting from a difference in the expansion of the glaze (body) and the colour,

mostly appear only at the third firing ; indeed, it frequently happens that the colours of a painting chip off, on this account, some time after this operation. To obviate this defect the chief thing to do is to ensure that the colours and body have an equal rate of expansion, so that the colours in cooling contract at the same rate as the body. Most frequently the chipping or cracking of the colours is due to defective methods of combination or preparation. The evil can never arise in the case of biscuit porcelain, since here the fusing of the glaze induces that of the colour, so that the expansion of the two becomes coincident and identical and they contract equally on cooling.

A good lookout must therefore be kept for all these phenomena, in order to prevent injuries, which are usually of a serious nature, and to this end it is necessary to become acquainted with the constituents of the glazes and their chemical action towards the colours in painting. This knowledge, however, can only be acquired by degrees, through practical working and prolonged experiment and experience.

There is still another factor exerting a considerable influence on the colours, namely, the action of vapours, especially the steam, carbonic oxide, and alkaline and lead vapours evolved in the muffle, which mostly produce ineradicable effects on paintings containing susceptible colours.

From numerous experiments made at Sèvres, it has been demonstrated that pure water in the condition of vapour is of itself incapable of exerting any injurious action on colours, provided the condensation of the steam be prevented by gradually increasing the temperature. No chemical action can therefore be in question here, the influence being mechanical when the moisture condenses on the painting in the form of small drops of water, which in trickling down convey some of the colour away. The precautions already

recommended in connection with the placing of the pieces in the muffle will prevent difficulties of this kind.

The case is, however, materially altered when the steam is mixed with carbonic oxide gas, the decomposing action of the latter being—as shown by Malaguti's experiments—greatly increased under these circumstances. Carbonic oxide exerts a powerful reducing action, especially on lead oxide.

Furthermore, sulphurous acid is very injurious in its action, a consideration necessitating the observance of extreme care in the washing (by boiling water) of reds prepared from ferrous sulphate, since, if any of the acid be left behind, the red colour will not assume its true lustre, and, moreover, the presence of sulphurous acid, even in small quantity, will rob the other colours of their beauty.

One observation of Brongniart's, in conclusion. He says : “ It is a common practice to add to blacks, when they are found to lack the proper tone, fairly large proportions of lampblack, without any injury to the vitrification resulting therefrom, so that carbon vapours penetrating into the muffle do no damage. In the case of wood fuel the conditions are different, the vapours from wood containing large quantities of empyreumatic oils and acids, and it is chiefly by these products that the muffle is ‘poisoned’. In this smoke the carbonic oxide gas is less to be dreaded than the pyroligneous acids present.”

CHAPTER XII.

REMARKS ON THE DIFFERENT METHODS OF PAINTING ON GLASS, PORCELAIN, ETC.

BEFORE the chemically prepared colours can be employed for painting, they must be brought into the finest state of division imaginable. This is effected by crushing and grinding, both these operations necessitating the exercise of the greatest care and attention, since it is only in this manner that a really fine and even coloration can be eventually obtained. It is in the highest degree important to preserve the colours, which are, for the most part, rather hard vitreous substances, from contamination by extraneous matters, by which they might be either hardened, softened or coloured.

Before proceeding to the grinding proper, the colours must be comminuted and ground half-fine in a clean porcelain biscuit (or, better, agate) mortar, the pestle being covered over with a piece of linen cloth and the pieces of colour pressed against the bottom of the mortar, where they are broken down to coarse powder.

The grinding is performed in two ways: in mills or on plates. The employment of mills, wherein the colour is ground along with water, allows of large quantities being treated at once, which means a considerable saving of time. The mills for our colours may only be composed of porcelain biscuit or hard glass; soft crystal glass is less to be recommended, since it makes the colours soft more readily than they can be rendered harder by the use of hard glass.

In Fig. 18 a section of a mill of simple construction is shown, this form being, on account of its capacity, still in general use.

i i is a kind of mortar with a conical projection (*a*) rising from the centre of the base and thereby forming a rounded annular channel in which rotates a cylinder (*b b, c c*), the lower part of which is rounded to fit the channel. This cylinder is higher than the sides of the mortar, and has a plate (*d*) of lead or other metal affixed to the upper end in order to increase the weight. The mill is worked by means of a handle (*e*).

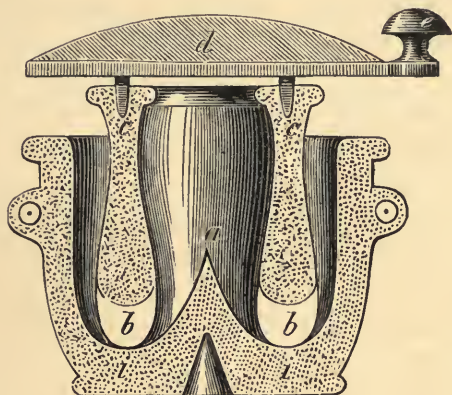


FIG. 18.

The colours may be brought into the finest state of division by grinding on quadrilateral glass plates; the rubbers or runners being made of porcelain or very hard glass. Soft glass is unsuitable by reason of its liability to erosion, whereby particles of glass find their way into the colour and increase its fusibility. A little water is always used in the grinding, and the colour is pushed towards the centre of the plate by means of a spatula of steel, ivory, or horn, the former being preferred, as less liable to wear. Besides, a trace of iron oxide is not specially injurious, even

to the most difficult colour, whereas ivory and horn spatulas wear out much quicker, and, by reason of the large proportion of calcium phosphate thereby introduced into the colour, the latter is easily rendered harder, and its fine vitreous lustre diminished. The spatula, whether of steel, horn, or ivory, should be used sparingly, and, indeed, only when absolutely necessary.

That in all these operations scrupulous cleanliness is necessary, will be apparent. When circumstances permit, it is better to have a separate mill for each colour, and in all other cases careful cleaning is essential. The grinding plates likewise require great cleanliness in manipulation. Both mills and plates should be cleaned by grinding powdered felspar or very pure white sand until the powder ceases to become coloured and remains perfectly white. The metals, gold and platinum, being prepared in the state of extremely fine powder, do not need grinding.

When the colours are finely ground they have then to be incorporated with oil, oil of turpentine being the medium corresponding most nearly to all the requirements of the case. The oil must, however, have been twice distilled, in order to get rid of every trace of resin, since this substance would carbonise in the firing and reduce the lead oxide in the flux. To facilitate the application of the colours, a certain quantity of thickened oil should be added to the oil of turpentine. This thickened oil can be obtained at any large colour vendor's where porcelain colours are sold, but, unfortunately, owing either to additions of resin or to having been heated too rapidly, is never in the desired condition, the result being that the colour is often not sufficiently tractable, but too quickly becomes viscid and dry. It is, therefore, preferable to prepare the thickened oil oneself, which can be done by filling a bottle with oil of turpentine and leaving it open and exposed to the sun, or behind the stove, for four to

eight weeks, whereby a pure clear, thick oil, highly suitable for painting purposes, will be obtained. This thickened oil should dissolve completely when mixed with oil of turpentine in any proportion. This result, however, is not always attainable in perfection, but only when the solvent turpentine is of the same kind as that from which the thickened oil was prepared.

Lavender oil, which is less volatile, may also be used instead of turpentine oil, but cannot be thickened like the latter. Olive oil, nut oil and poppy oil are also occasionally employed, but must be in the fresh state, since if in the slightest degree rancid, the colours run apart and vanish.

There are three general methods of applying the colours, *viz.*, with the brush, the stippling brush, and by dusting. Colours and metals are mostly applied on glazes by means of the brush, and, in order to facilitate the application over such a smooth surface, and to render the colours more adherent, a coating of oil of turpentine is first laid on; only when the colour has begun to dry and thereby acquired a sufficient degree of tenacity can it be brushed over.

The stipple is a kind of brush the hairs of which, instead of being arranged to form a fine point, are cut off evenly at the end like a broom. It is chiefly employed when it is desired to cover a large surface over with a single colour in one piece with as even distribution as it is possible to attain. This can scarcely be done by means of the ordinary brush, or only with the greatest difficulty, since the repeated strokes can easily be seen, and therefore fail to produce a perfectly even and uniform surface of colour.

The colours employed for the production of ground-works by this means must be somewhat thicker than those for painting, and to this end they are set, after mixing, in a warm place for some time to thicken. The colour is laid on with an ordinary brush and then distributed with the

stippling brush until the surface is covered with a perfectly uniform and smooth coating of colour. In the case of large surfaces coated with a single colour, two applications are necessary to ensure a proper effect.

Dusting is practised only for earthenware and in such cases where the colour is to be applied rather thickly, or where, on account of its vitreous nature, it cannot be laid on regularly with the stippling brush.

The piece to be dusted must be coated over, on the parts to which the dry powdered colour is to be applied, with a layer of some adhesive material, whereby the colour is retained and stuck fast. The medium employed (formerly the most remarkable and complicated preparations were used) is generally linseed oil, but, according to Brongniart, nut oil is decidedly preferable. The oil in question is boiled with a little litharge, to increase its drying properties, and brought to the consistency found advisable in practice. It is then applied to the surface and distributed thinly and evenly thereon by means of a brush, which is easy of performance, the oil not being colourless. Then the finely powdered dry colour is placed in a silk sieve of the requisite fineness and the surface in question dusted over with the sifted colour, which adheres to the coated portions, but is easily removed from the remaining parts by the aid of a dry brush.

The colours and metals for (fired) unglazed biscuit, which has a dull surface, are, for the most part, merely mixed with water.

A closer consideration of the application of colours to glass is of importance. The methods employed are: either to take a single sheet of clear glass and fire the whole of the colours and shadings on to this, or else a picture is formed by laying a number of pieces of coloured glass side by side and, since these form the various local colours, merely painting the outlines and shadows thereon; this latter method is termed

“mosaic” glass painting. More rarely the two methods are combined in the one picture by forming the latter partly of coloured sheet glass and partly of painted clear glass.

To paint glass on one side—the so-called *peinture en apprêt*—the following rules should be observed: For this purpose a clean, clear sheet of very refractory glass, free from air bubbles, is selected—since the whole of the artist’s trouble would be wasted if he attempted to paint on glass more readily fusible than the colours themselves. On the other hand, it is possible, as was done by the ancients, to produce fine effects on what is apparently the most impure and common of glass, provided it does not contain too much lead.

Before painting, the glass should be thoroughly cleaned by being well rubbed over with pure lime broken down by exposure to the air. The sheet is then covered with a foundation, to which end some glass painters apply an even coating of oil of turpentine with a brush or clean cloth, whilst others use a clean black pigment, which, however, does not deprive the glass of its transparency, but at most gives it the appearance of a dull ground surface. Both methods serve to produce an adherent surface which will take on the design and the colours better than the untreated glass, and the second of the two also prepares the glass for some of the effects it is intended to develop in the painting. In both cases the coating must be applied with great care and dried quickly in a manner to exclude dust, etc. For painting on a single sheet only one cartoon is required, but this can be copied in two different ways.

Either the coated and dried sheet is laid over the cartoon and the outlines of same traced on the surface of the glass with a lead pencil or any suitable glass colour, or else the cartoon is laid upon the sheet and all the outlines are gone over with a steel or ivory point. If, in this latter

method, the glass has only been coated with oil of turpentine, the back of the cartoon must be covered over with blacklead so as to produce an impression of the outlines on the glass surface. In any event the cartoon, whether on or under the glass, must be fastened with a little wax on each of the four sides to prevent slipping.

The painting is performed by laying the glass on a desk, consisting of a sheet of glass in a wooden frame, which can be made to slope by means of supports at the sides. A transparent desk is necessary to allow the daylight to shine through the work. The sheet in work can also be removed from the desk when desired and laid on a piece of white paper, whereby it will be easier for the painter to judge of the effect of certain colours.

Enough has already been said with regard to the grinding and mixing of the colours ; the following remarks, however, are specially applicable to glass painting.

The fluxes, *i.e.*, those pigments containing the oxides in a fused and vitrified condition in the flux, and themselves constituting transparent glasses, should only be coarsely granulated before application, since, in proportion as they are ground fine, the less transparent and perfect do they appear when fired.

Such pigments as are applied merely in admixture with an earthy medium and without any flux, as, for example, the reds and yellows prepared from silver, are not ground with oil, but merely stirred up to a thick gruel in water and applied to the glass.

Whilst the ordinary glass colours are laid on with the brush, the stipple being used to cover large surfaces, the silver colours are applied by means of a spatula, the thickness of the coating being about that of the back of a knife. The most difficult operation is the laying on of the flux, which must be applied in the condition of a viscid mass,

sufficiently moist to flow but consistent enough to cover the glass. This is, however, effected by applying small portions with the brush or by a spoon, spreading them out with the instrument, and then inclining the glass in different directions so that the surface becomes covered without the liquid flowing over the edge of the design.

If it is desired to deepen the tone in places, it is only necessary to induce a thicker aggregation of the flux by holding the glass in an inclined position a while.

The remaining rules for the application of pigments are, more or less, results of the different methods of painting on one sheet, of which there are three principal :—

Either the whole of the picture, with its outlines and shadows, is drawn on one surface of the glass with black, brown, or grey colour, and the divisions illuminated by colours applied to the under surface; or else the painter imitates the method of painting in oils; or, finally (and this is most usual), the two methods are combined, each being carried out where it will produce the desired effect. According to Geffert, the chief points to be observed in all cases are as follow :—

The shadows and outlines in dark colours, as well as what constitutes groundwork in oil painting, are painted on the side next the observer, the whole of the illuminating colours and fluxes, especially the principal shades, being laid on the back.

Intermediate tints, gradations, and transition colours are, as a rule, applied on the front surface, but also sometimes at the back, in case they are unsuitable for application together on the one surface by reason of their running together and producing a discordant colour.

The reds and yellows from silver are always applied to the back of the glass.

In individual instances colours are laid on in correspond-

ing situations, both front and back, in order to produce particular shades from the harmonising of the colours by transmitted light. So, for example, purple on one side and silver on the other give a beautiful scarlet colour ; blue and yellow will give, according to their relative intensity, the various shades of green ; and green, again, by the interposition of blue, can be regulated for the finest distant effects. In this manner, by means of various combinations, and by mixing the colours, the most diverse effects can be produced.

When it is desired to apply colours to a surface already painted, *e.g.*, outlined, the previous colour must be dried by moderate and regular warmth. The yellows, which, as we know, do not contain any flux, but are merely mixed with ferruginous clay, should not at any time be laid over many other colours, not even black shadows, unless the same have been already fired. The glass colours may be somewhat deeper than those for oil painting, since they lose some of their intensity when fired.

If the colour has been applied over the edge of the design or section, the excess may be removed with the knife when dried.

Special effects of light and shade can be developed by removing small portions of the colour with a graver of fine grained wood, pointed in front and smooth behind, a process practised from the earliest times.

It is inadvisable to leave the painted glass to stand for long ; one or two days are quite sufficient to ensure thorough drying, and any delay thereafter is injurious.

The process of mosaic painting has been briefly described already and further particulars have no interest for us, since this process is only a question of grouping coloured glasses together. The painting of porcelain has been referred to at the commencement ; all the colours applied by the brush vitrify, when fired, much better than those that have been

stippled. The main object of porcelain painting is to have the colours lustrous and well vitrified, permanent and of good appearance. Each painting must undergo at least two firings, and, occasionally, when it is desired to impart the utmost possible completeness, three; and it also happens, on occasion, that a painting is fired four, and even five times; of course, such a piece is more exposed to damage than others.

A good painter does not require every colour, but can arrange satisfactorily with a certain number only.

The subjoined table (by Salvétat, Strele) shows the arrangement of a colour palette for figures, and being of the simplest, is therefore extremely suitable for beginners. It is prepared by taking a square sheet of glass, under which is fastened a piece of white paper with the numbers of the colours marked in ink, each heap of colour being placed over its corresponding number. Whilst the nineteen colours arranged round the three outer sides of the palette are quite sufficient for the requirements of the figure painter, the twelve others in the centre are intended as supplementary colours for the landscape and flower painter, these subjects requiring a larger number of shades of green and blue, as well as the gold colours.

Care is necessary to apply the colours gradually, thinly and regularly, and not to spread them on too thick, since, in the latter case, the risk of chipping off will be incurred. Care is equally necessary that all the colours used for one firing should be of equal fusibility. The practice of painting the lighter portions with soft, and the shadows with hard colours, must be specially avoided. Should such an error be committed in the first firing it is difficult to remedy.

Certain full, powerful tones can only be obtained by laying one colour over another. This applies particularly to violets, deep shades of which can only be produced by means

Dark grey 6	Dark iron-violet 7	Pale iron-violet 8	Reddish grey 9	Blood red 10	Lake red 11	Carmine iron-red 12	Flesh red 13	Pale yellow 14	Ochre yellow 15	Orange red 16	Wood brown 17	Sepia brown 18	Brown- green 19								
Brownish black 5	<table><tr><td>Fusible carmine</td><td>Purple</td><td>Gold violet</td><td>Dark green</td></tr><tr><td>Emerald green</td><td>Bluish green</td><td>Dark blue</td><td>Dark yellow</td></tr><tr><td>Light yellow</td><td>Pale yellow for green and blue</td><td>Ochre yellow for brown</td><td>Fusible grey</td></tr></table>								Fusible carmine	Purple	Gold violet	Dark green	Emerald green	Bluish green	Dark blue	Dark yellow	Light yellow	Pale yellow for green and blue	Ochre yellow for brown	Fusible grey	
Fusible carmine	Purple	Gold violet	Dark green																		
Emerald green	Bluish green	Dark blue	Dark yellow																		
Light yellow	Pale yellow for green and blue	Ochre yellow for brown	Fusible grey																		
Bluish grey 4	Ultra- marine blue 3	Sky blue 2	Bluish green 1																		

of a priming of red or brown ferric oxide colours, firing in this ground and then vitrifying with a second firing with purple or violet gold colours; carmine is unsuitable for this purpose, the entire colour being thereby destroyed.

The task of painting a red cone, for example, is performed, according to Brongniart, as follows : A commencement is made by colouring in the lighter portions with blood red and light yellow for carnation, the half tints being worked in with pure blood red, the half tints of the shadows with blood red and reddish brown, and the darkest parts with the same colours deepened with sepia brown. In this manner a finished object is produced, the colours of which have been obtained by toning and not by the thickness of the colour, and there is no danger of the colour chipping off. If this painting be coated with purple before the second firing, an amaranthine cone is obtained. Only by applying the more fusible colours by degrees can loss of lustre be avoided.

The blending of the colours themselves can only be learned by experience and prolonged practice. It is impossible to lay down any definite regulations therefor, since different bases and perceptions manifest themselves in almost every picture. The so-called discord of colours is mostly due to defective blending or to reactions occurring when one colour has been applied over another.

The foregoing general prescriptions and observations will, it is anticipated, suffice to enable the beginner to steer clear of the more glaring defects ; other particulars can only be acquired by continual practice and experiment, by obtaining a practical knowledge of the colours, studying the blending of same, and then proceeding to practise with the brush and with monochrome paintings.

APPENDIX.

CLEANING OLD GLASS PAINTINGS.

C. CUNO, who, from 1857 to 1867, was charged with the erection of the principal church of the Lower Rhine Province, the cathedral of Xanten, had, in the course of his task, occasion to test various methods of renovating old glass paintings. The first to be tried was Grund's method, but this was unsuccessful. The glass panes, after exposure for several weeks in a perforated chest to the action of the tail-race water from a mill, were found to be cleaned externally, but the crust formed on the glass by the action of incense, dust, and probably also by chemical change in the glass itself, was left untouched. Rings (a glass painter) cleaned old panes by washing with black (green) soap, repairing the damaged painted outlines of the pictures, and fired the glass again, scraping off the white crust formed during this operation. The appearance of the pictures so treated was, however, unsatisfactory, being yellow and cloudy. Tinnefeld exposed the panes to the action of a solution of sodium chlorate for several days, and then to very dilute hydrochloric acid. If a favourable result did not ensue the glass was next treated with a mixture of unslaked lime and black soap and rinsed in cold water.

The author proceeds to clean old glass paintings by first subjecting them to a prolonged swilling by a jet of water, to remove dust, as far as possible, by mechanical means. Next follows a washing with very dilute caustic soda and a

thorough rinsing, this treatment being, when necessary, several times repeated, and followed—if the colours do not by this time show up in a satisfactory manner—by other washings with dilute nitric acid (1 part nitric acid to 4 parts water), a rinsing with water being performed after each operation.

By this means old glass paintings, so contaminated as to appear perfectly black, have been completely restored.

INDEX.

A.

Agate blue, 190.
 Alabaster glass, 13.
 Albite, 80.
 Alumina lustre, 241.
 Aluminium glass, 12.
 Antimony, butter of, 231.
 — oxide, 22.
 Arita enamel, 200.
 Azure blue, 190.

B.

Barium chromate, 25.
 Beni, 200.
 Biscuit, 16.
 — porcelain colours, 207.
 Bistre brown, 173.
 Black colours, 180.
 — flux, 2.
 — glass, 148.
 "Blind" glass, 14.
 Blue colours, 117-123, 157-161, 188.
 — glasses, 143.
 — violet, 171.
 Bolley, P., 44.
 Boracic acid, 88.
 Borax, 87.
 Böttger, J., 15.
 Bottle glass, 12.
 Brongniart, 8, 31.
 Brown coloured glasses, 142.
 — colours, 123-127, 173, 187.
 Buisson, 43.
 Bunel, 43, 180.
 Burgos lustre, 233.
 Burnished gold, 235.

C.

Calamine, 63.
 Cantharides lustre, 239.
 Capaun, 46.

Caput mortuum, 35.
 Carré's lustre gilding, 232.
 Chestnut brown, 173, 203.
 Chrome brown, 176.
 — yellow, 26.
 Chromic oxide, 29.
 — — from ammonium
 chromate, 31.
 Chromic oxide from potash and
 sulphur, 29.
 Chromic oxide, wet method of
 preparing, 31.
 Chromic oxide from mercurous
 nitrate and potassium chro-
 mate, 32.
 Cleaning old glass paintings, 295.
 Cloisonné enamel, 18, 227.
 — — flux, 228.
 Cobaltous silicate, 55.
 Cobalt oxide, 13, 51.
 — protoxide, 51.
 Colombines, 16.
 Coloured glasses, 139.
 Colour pastes, 132.
 Colours for glass painting, pre-
 paring, 90.
 Colours for glass painting, black,
 90.
 Colours for glass painting, red, 94.
 — — white, 93.
 — — yellow,
 101.
 Contraction of colours, 278.
 Copper oxide, 13, 48.
 — protoxide, 49.
 — ruby glass, 146.
 Crystal glass, 12.
 — — Bohemian, 12.

D.

Dead gold, 234.
 Deck, Th., 220.

Delong, 33.
 Deutsch, H., 243.
 Devitrification, 14.
 Dull lustre, 234.
 Dutailly, 201.
 Dutertre's lustre gilding, 231.

E.

Earthy colours, 68.
 Ehrlich, F. L., 236.
 Enamel, 17.
 — cloisonné, 18, 227.
 — compressed layer on glass, 242.
 Enamel, coloured, 226.
 — colours, 216.
 — for artistic work, 223.
 — mass colouring, 17.
 — opaque, 218.
 — translucent, 226.
 — transparent, 216-218.
 Encaustic painting, 9.

F.

Faience, 20.
 — colours, 206.
 Felspar, 80.
 Ferrous chromate, 40.
 Firing the colours, 244.
 — — glass colours, 244.
 — — porcelain colours, 248.
 Fitch, W. B., 227.
 Flash glass, free from lead, 147.
 Flashing glass, 5.
 Fluxes, 79, 127.
 Fremy, 47.
 Frit, 12.
 Fuchs, Dr., 45.
 Fuss, 145.

G.

Glass, 11.
 — French, 12.
 — "charge," 12.
 — colouring, 13.
 — colours, firing, 244.
 — gilding, 236.
 Glasses, yellow coloured, 141.
 Glass-makers' pipe, 12.
 Glass-painters' colours, 10.
 — fluxes, 10.
 Glass painting, history of, 1.
 Gold, 73.

Gold, fulminate, 231.
 — lustre, 233.
 — purple, 41.
 — ruby glass, 145.
 Green-blue, 190.
 Green coloured glasses, 143.
 — colours, 107, 164, 187.
 Grey colours, 176, 187, 196.
 Grinding mill, 283.
 — plates, 283.
 Groundworks, producing, 287.

H.

Hecht, H., 235.
 Horn silver, 29.

I.

Indigo blue, 192.
 Iridium grey, 179.
 — oxide, 46.
 Iron oxide, 34.
 — — for fine (red) colours, 38.
 — — from ferrous sulphate, 36.

Iron red, Vogel's, 40.
 Italian earth, 70.

J.

Jean, 33.
 Jewellery, white enamel for, 224.

K.

Kaga red, 200.
 Kaolin, 15.
 Klaproth, 29.
 Kunkel, J., 7.

L.

Lead antimoniate, 23.
 — chromate, 26.
 Litharge, 89.

M.

Mahogany brown, 70.
 Majolica glazes, 202.
 Malaguti, 50.
 Manganese oxide, 60.
 — — for violet, 172.
 Mars orange, 72.
 — red, 72.
 — yellow, 71.

Metallic ornamentation, 230.
— pigments, 22.

Metals, 73.

Minium, 89.

"Mosaic" glass painting, 287.

Mother-of-pearl lustres, 240.

Mouse-grey, 177.

Muffle colours, hard, 186.

— — soft, 152.

Muffles, 253.

Mussel gold, 74.

— silver, 76.

N.

Nankin yellow, 175.

Naples yellow, 23.

Noble metal decorations on earthenware, 236.

O.

Ochre, red, 70.

— yellow, 68.

Orthoclase, 80.

Osmium, 46.

P.

Peinture en apprêt, 287.

Pernettes, 16.

Pigments, 22.

Pink red, 202.

"Pink salt," 44.

Pitch blende, 62.

Platinum, 77.

— grey, 179.

— lustre, 241.

Polishing, 277.

Poreelain, 14.

— composition of colours for, 149.

Porcelain, true, 189.

— — colours for, 189.

— earth, 15.

— gilding, 230.

— glazes, coloured, 204.

Potash felspar, 80.

— glass, 11.

Potash-lead glass, 12.

Potassium carbonate, 88.

Pratt, J., 238

Presbyter, 2.

Preussler, W., 242.

Purple, dark, 169.

— light, 168.

Purple of Cassius, 43, 210.

Pyrometer, 216, 251.

Q.

Quartz, 81.

— purifying, 84.

— quenching, 86.

— washing, 85.

R.

Red coloured glass, 144.

— colours, 152, 186.

— underglaze, 214.

Red-violet shades, 170.

Robert, P., 43.

Rocaille flux, 89.

Rose Dubarry, 198.

Rouailler, 197.

Ruby glass, 13, 145.

— — lead, 147.

S.

Salvétat, 8.

Salvétat's grey flux, 177.

Schierholz, A., 242.

Schnorr, 15.

Sepia brown, 175.

Sèvres porcelain, 8.

Silver ehloride, 27.

Smalt, 13, 54, 57.

Soda, 88.

— felspar, 80.

Soda-lime glass, 12.

Staffordshire lustre, 233.

Steinbreeht, 214.

Stoneware, 19.

— colours, 206.

— glaze frit, 203.

— mass, blueing, 209.

Strong fire, colours for, 189.

— glazes, 201.

T.

Terra di Sienna, 70.

Test sherds, 249.

Teuchner-Klösterle, 234.

Tin oxide, 13.

Titanie acid, 193.

Transenamel, 216.

Tungstic acid, 196.

Turquoise blue, 118, 119, 158, 159,

160, 191, 213, 221, 227.

U.

Umber, 71.

Uranium oxide, 62.

V.

Vauquelin, 29.

Violet, 111.

— glass, 148.

Vogel's iron red, 40.

W.

White colours, 183.

Witherite, 25.

Y.

Yellow, art, 6.

Yellow-brown colours, 187.

Yellow colours, 68, 101, 161.

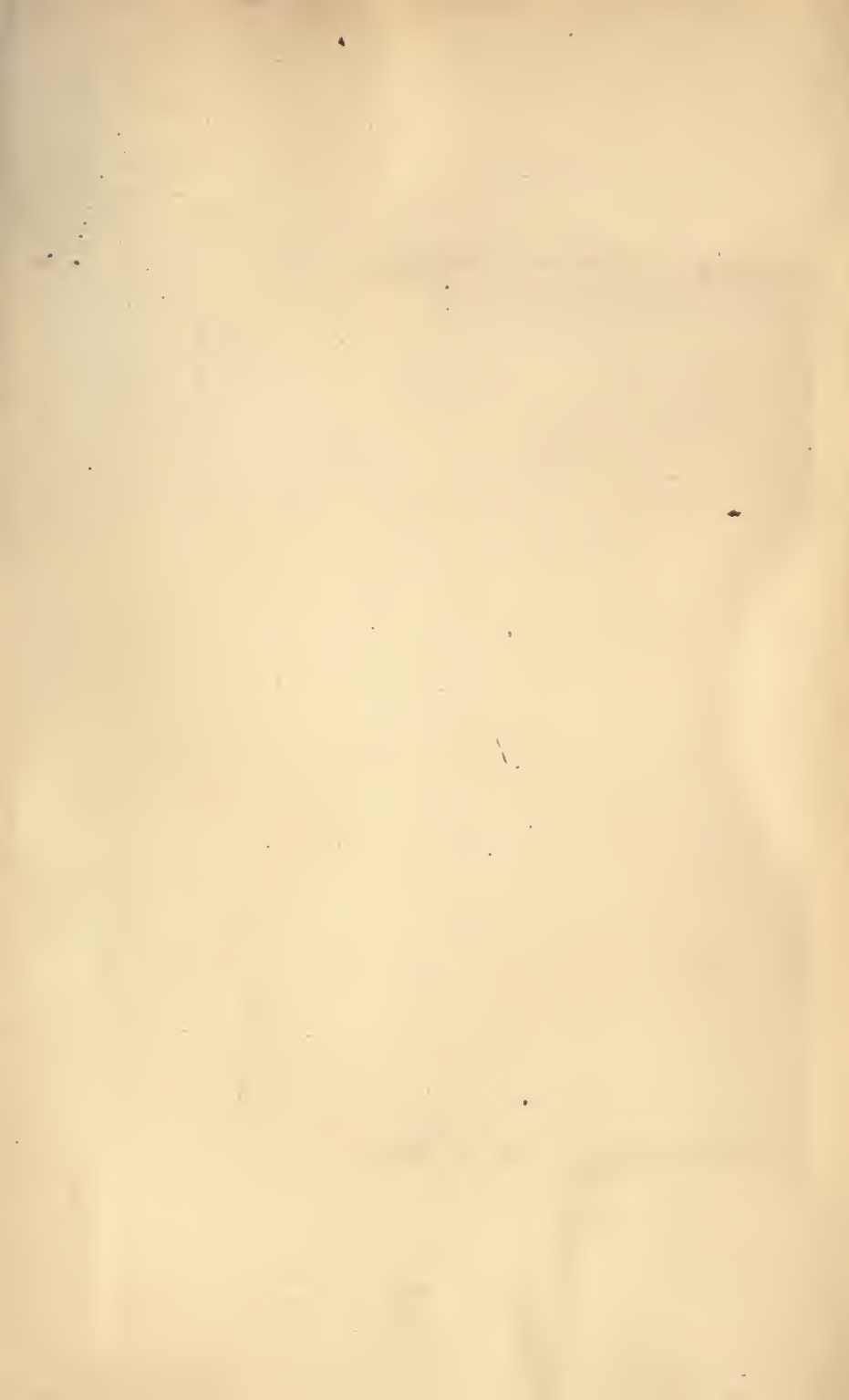
— — for strong fire, 195.

Z.

Zaffre, 59.

Zinc oxide, 63.

— phosphate, cobaltous, 56.



TC
H

378540

Hermann, Felix

Painting on glass and porcelain and
enamel painting; tr. by C. Salter.

**University of Toronto
Library**

**DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET**

Acme Library Card Pocket
LOWE-MARTIN CO. LIMITED

